

# Petroleum Drilling Fluids as a Source of Mercury to the Offshore Environment

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# Today's Topics:

... based mainly on data from the Gulf of Mexico.

1. Hg in drilling fluid.

2. Total Hg and **Methyl Hg** in sediment near drill sites.

3. Hg in biota near drill sites.

4. Overview of drilling sources of Hg.

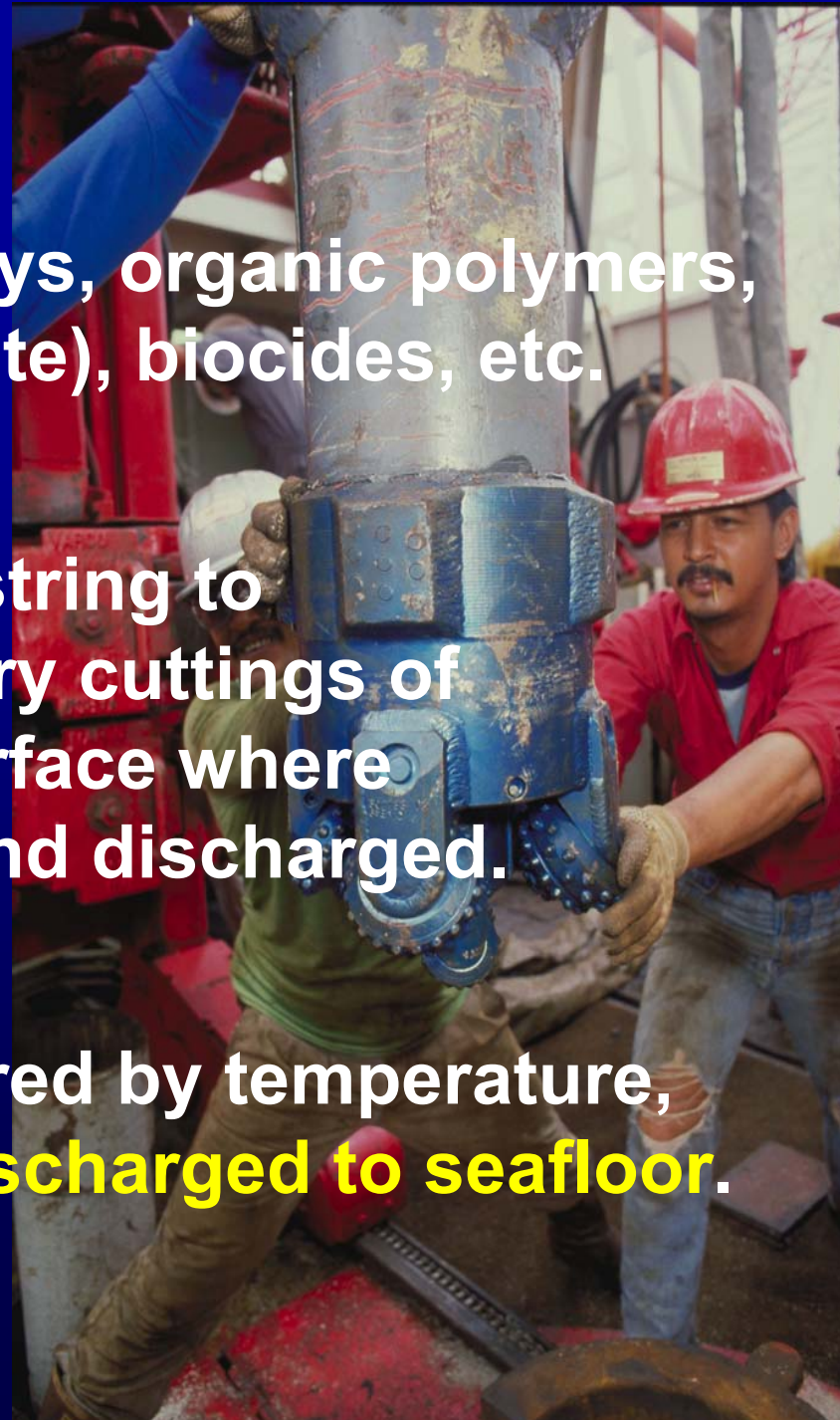


# Drilling Fluids

Formulated mixtures of clays, organic polymers, weighting agents (e.g., barite), biocides, etc.

Circulated through drill string to lubricate drill bit and carry cuttings of sediment and rock to surface where cuttings are separated and discharged.

Drilling fluids used until altered by temperature, pressure, chemistry; **then discharged to seafloor.**



# Hg in Drilling Fluid Solids

**<10 ng/g to 3,000 ng/g (ppb)**

[i.e., <0.01 to 3 µg/g (ppm)]

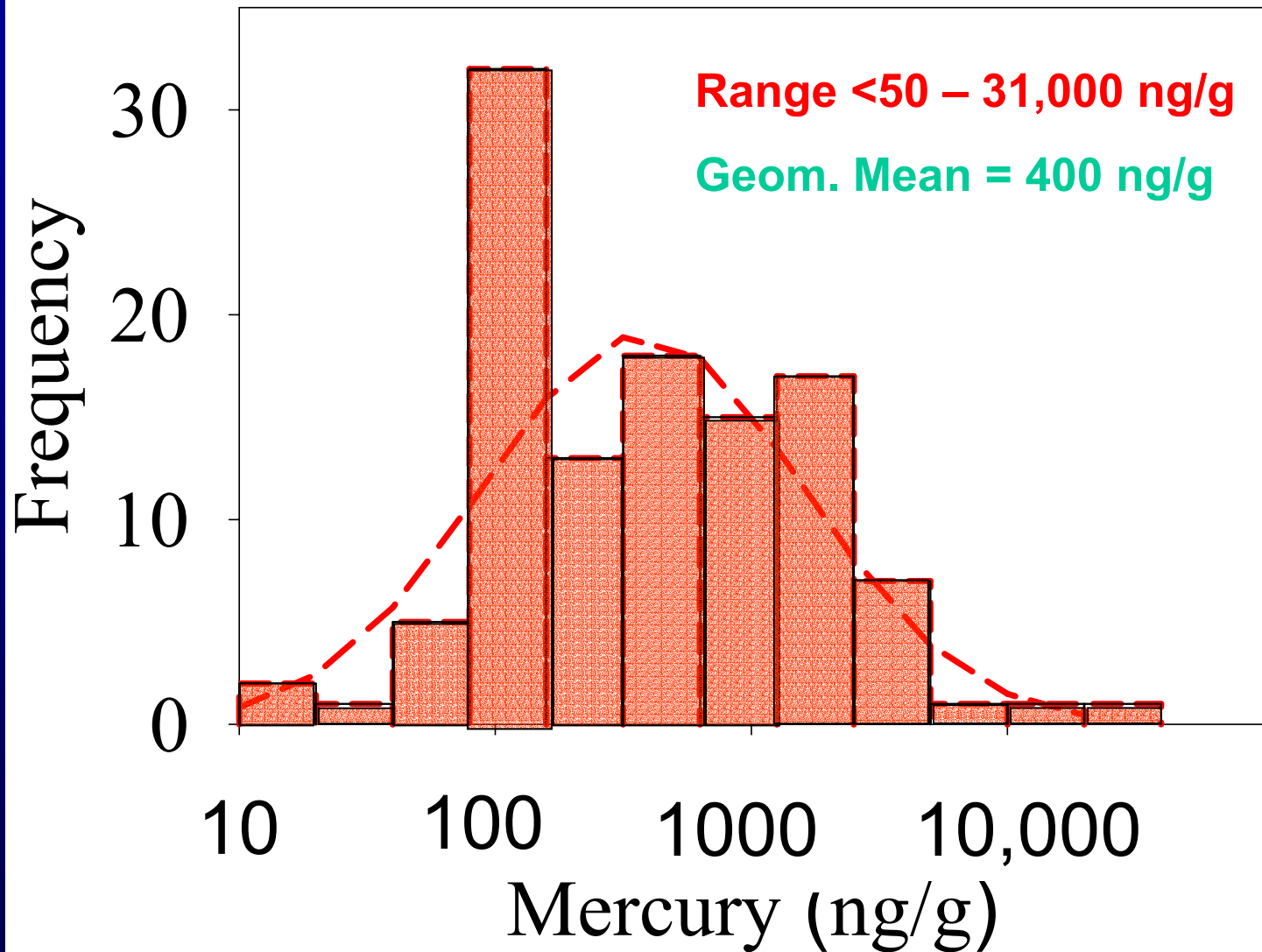
...relative to background  
levels of Hg in sediment  
of **5 to 100 ng/g**

Hg levels in drilling  
fluid are directly  
related to levels of  
barite ( $\text{BaSO}_4$ ) – the  
primary source of Hg  
in the fluids.



# Total Hg in barite ( $\text{BaSO}_4$ )

Hg is a natural impurity in barite and is not directly added to drilling fluids.

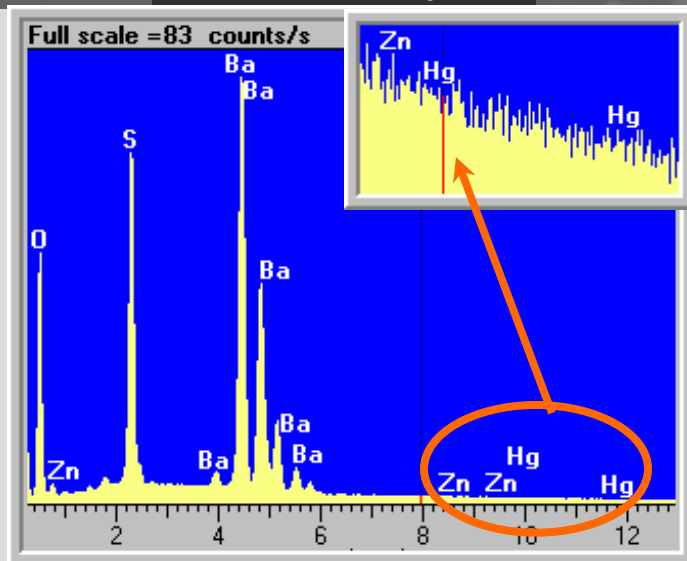
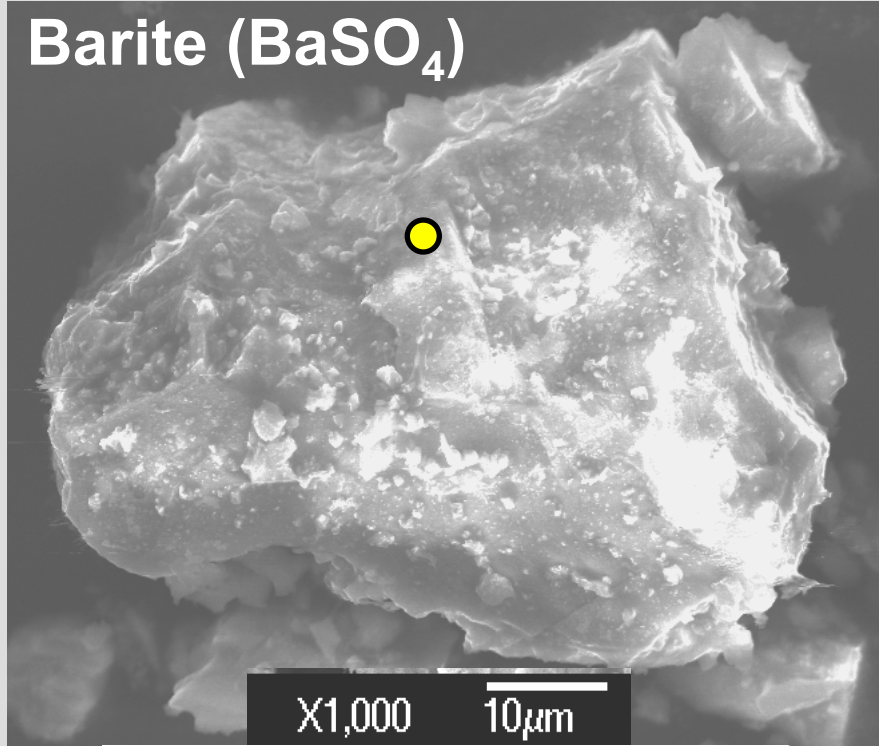


(Candler et al., 1992)

**EPA (1993) set limit for Hg in barite @1000 ng/g (1 ppm).**

# Hg in drilling fluid barite.

Barite ( $\text{BaSO}_4$ )

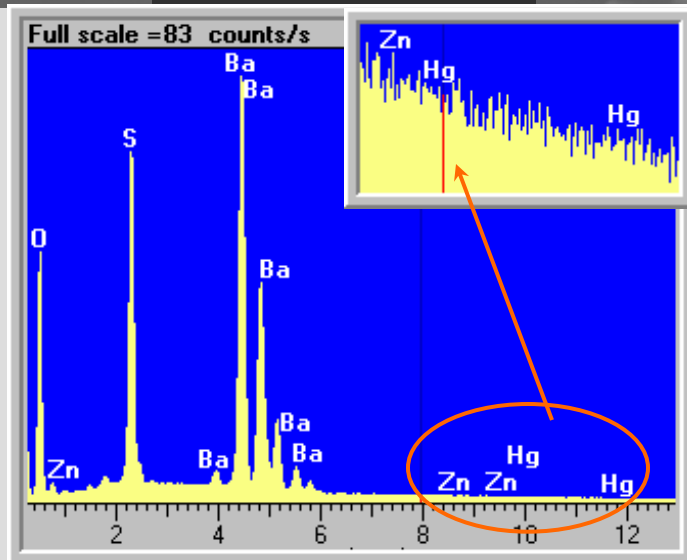
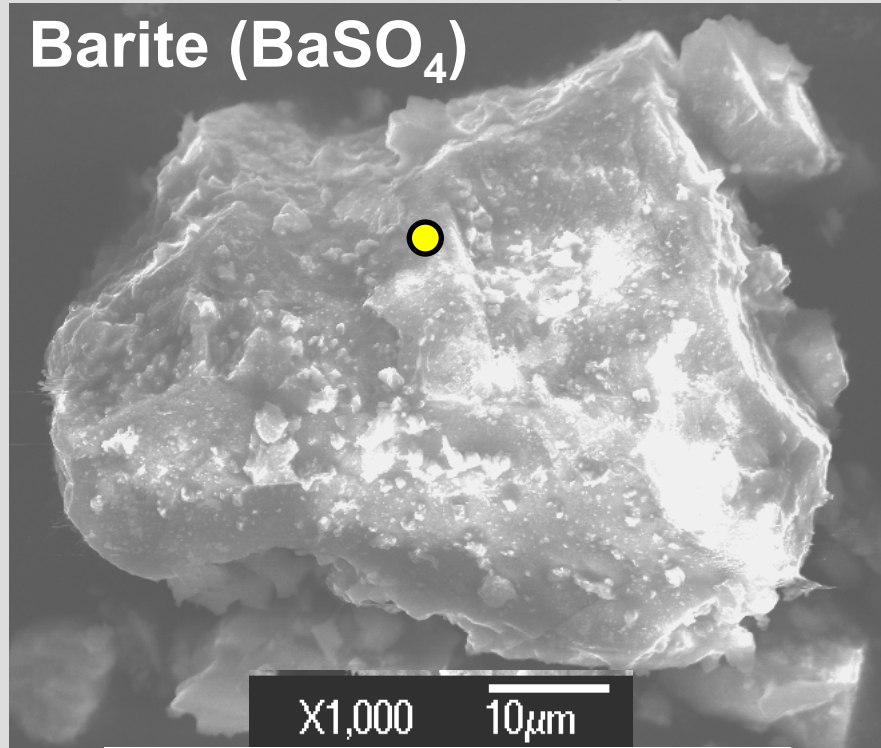


keV

Courtesy of Joe Smith, Exxon-Mobil

# Hg in drilling fluid barite.

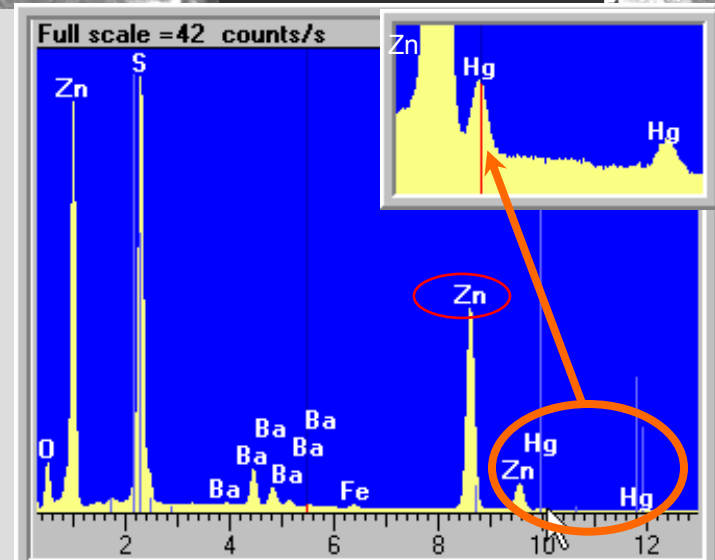
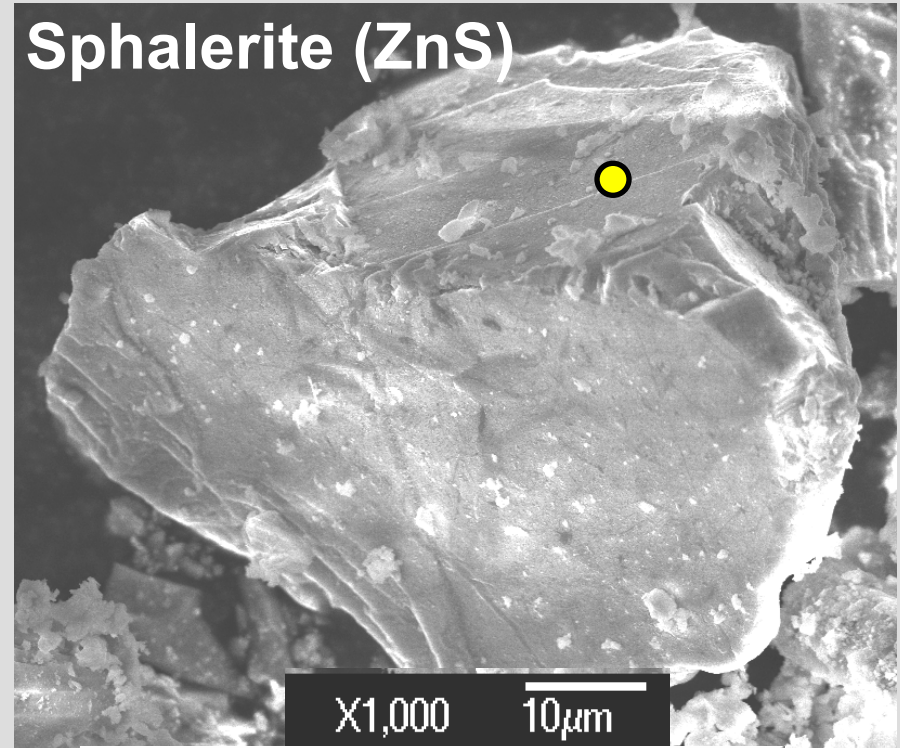
## Barite ( $\text{BaSO}_4$ )



keV

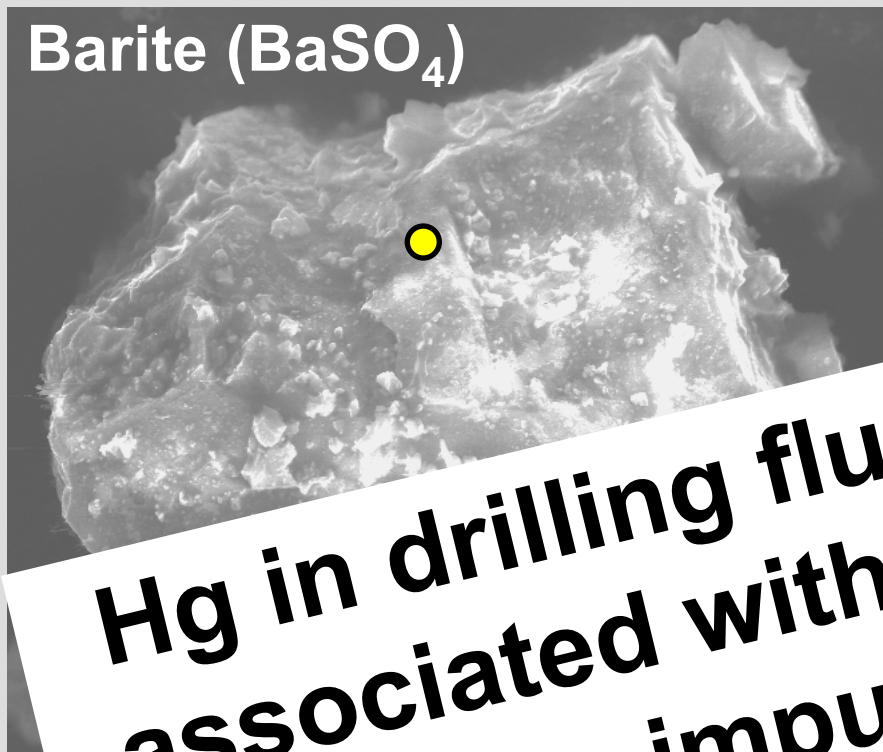
Courtesy of Joe Smith, Exxon-Mobil

## Sphalerite ( $\text{ZnS}$ )



keV

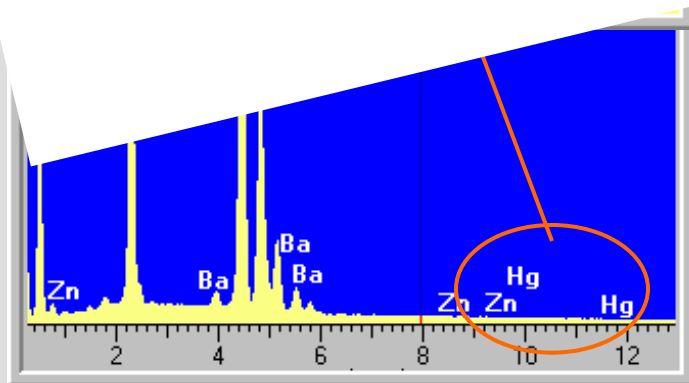
Barite ( $\text{BaSO}_4$ )



Sphalerite ( $\text{ZnS}$ )

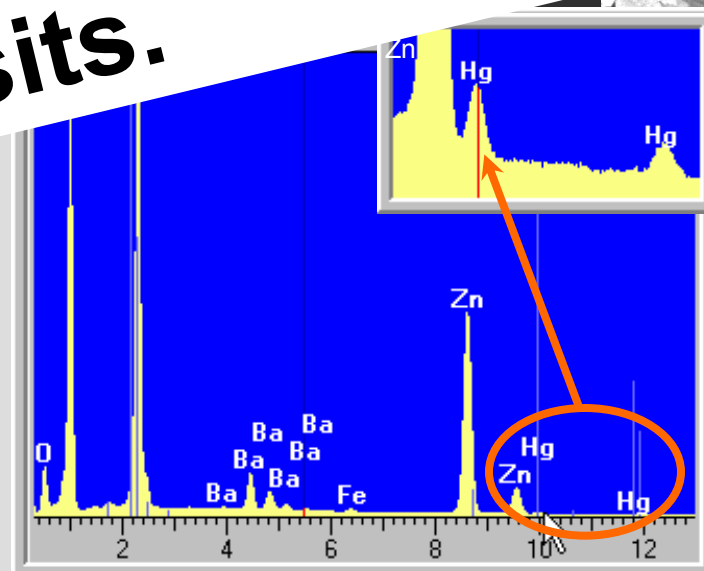


**Hg in drilling fluid seems to be associated with sulfide phases that are impurities in barite deposits.**



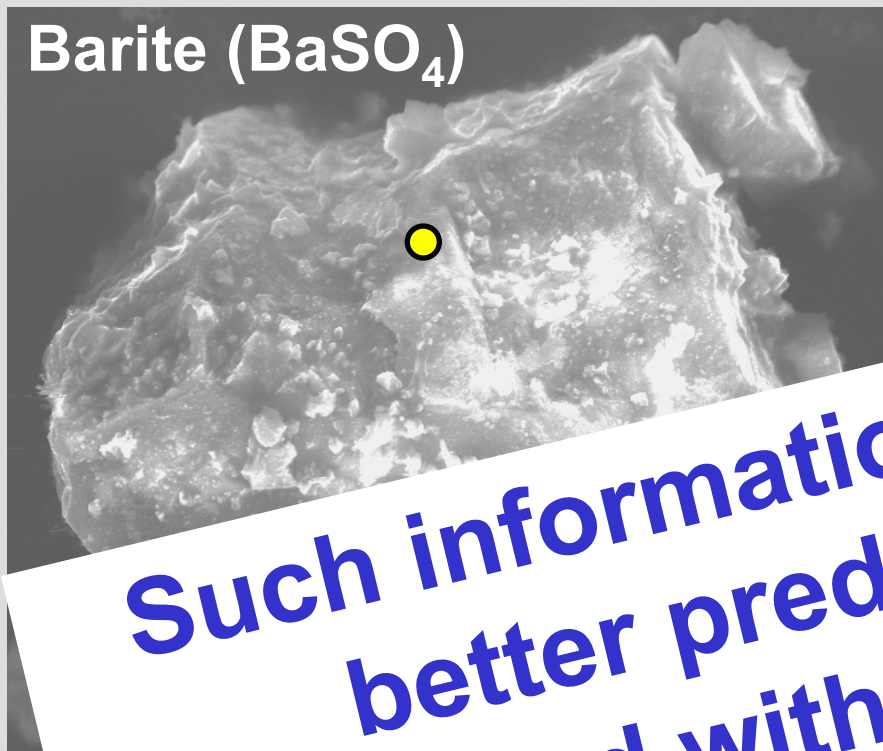
keV

Courtesy of Joe Smith, Exxon-Mobil

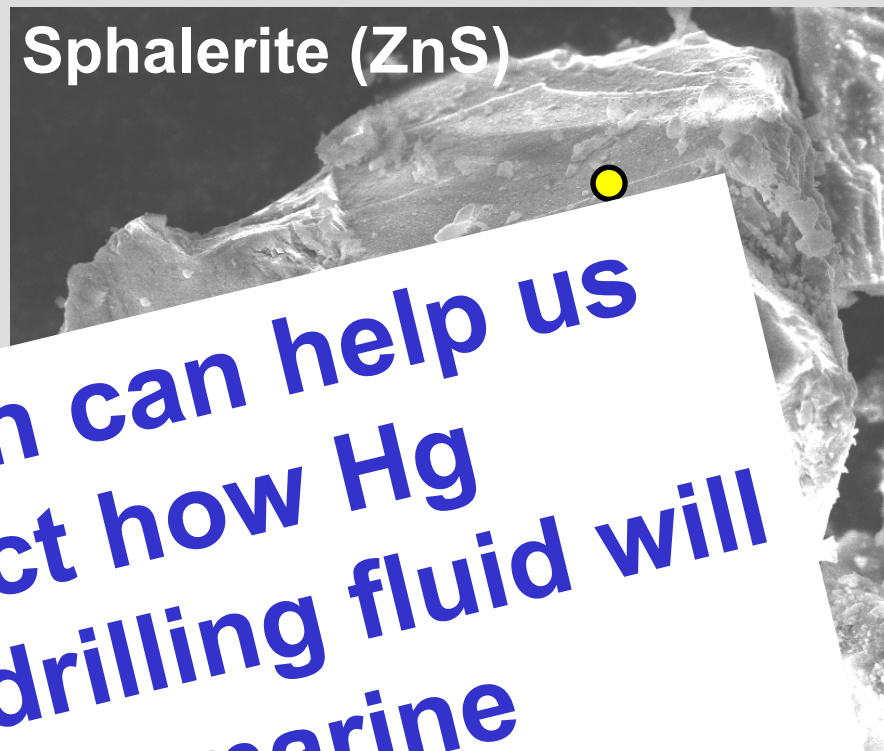


keV

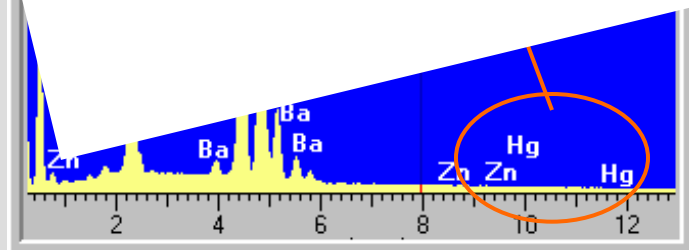
Barite ( $\text{BaSO}_4$ )



Sphalerite ( $\text{ZnS}$ )

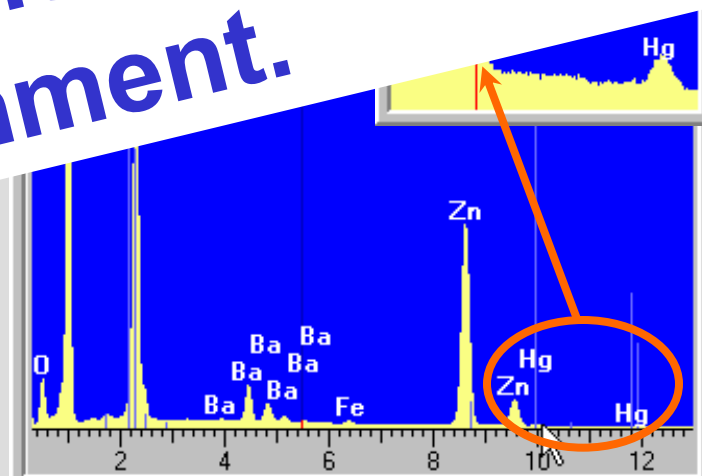


Such information can help us better predict how Hg associated with drilling fluid will behave in the marine environment.



keV

Courtesy of Joe Smith, Exxon-Mobil

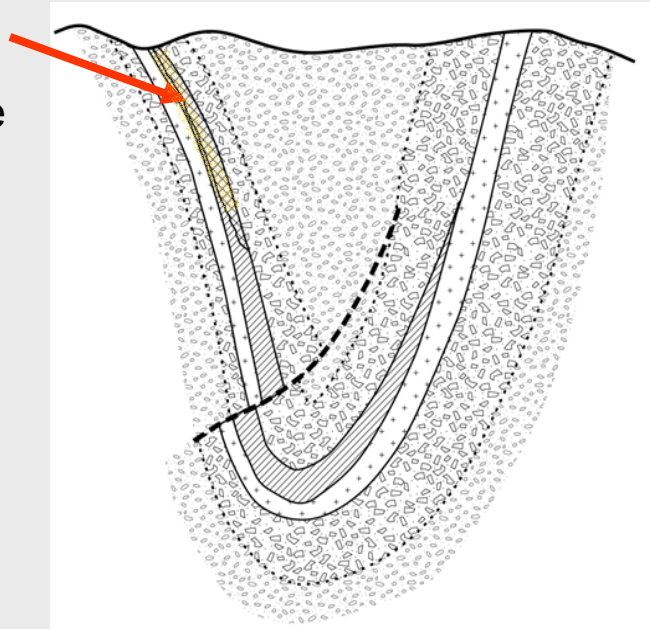


keV

# Barite and Sulfide Minerals in Vein Deposits

Barite-  
pyrite-  
sphalerite  
ore

Metamorphosed  
Sedimentary Setting -  
Australia\*



Dolomitic



Pyrite-  
Sphalerite-  
Galena



Sideritic

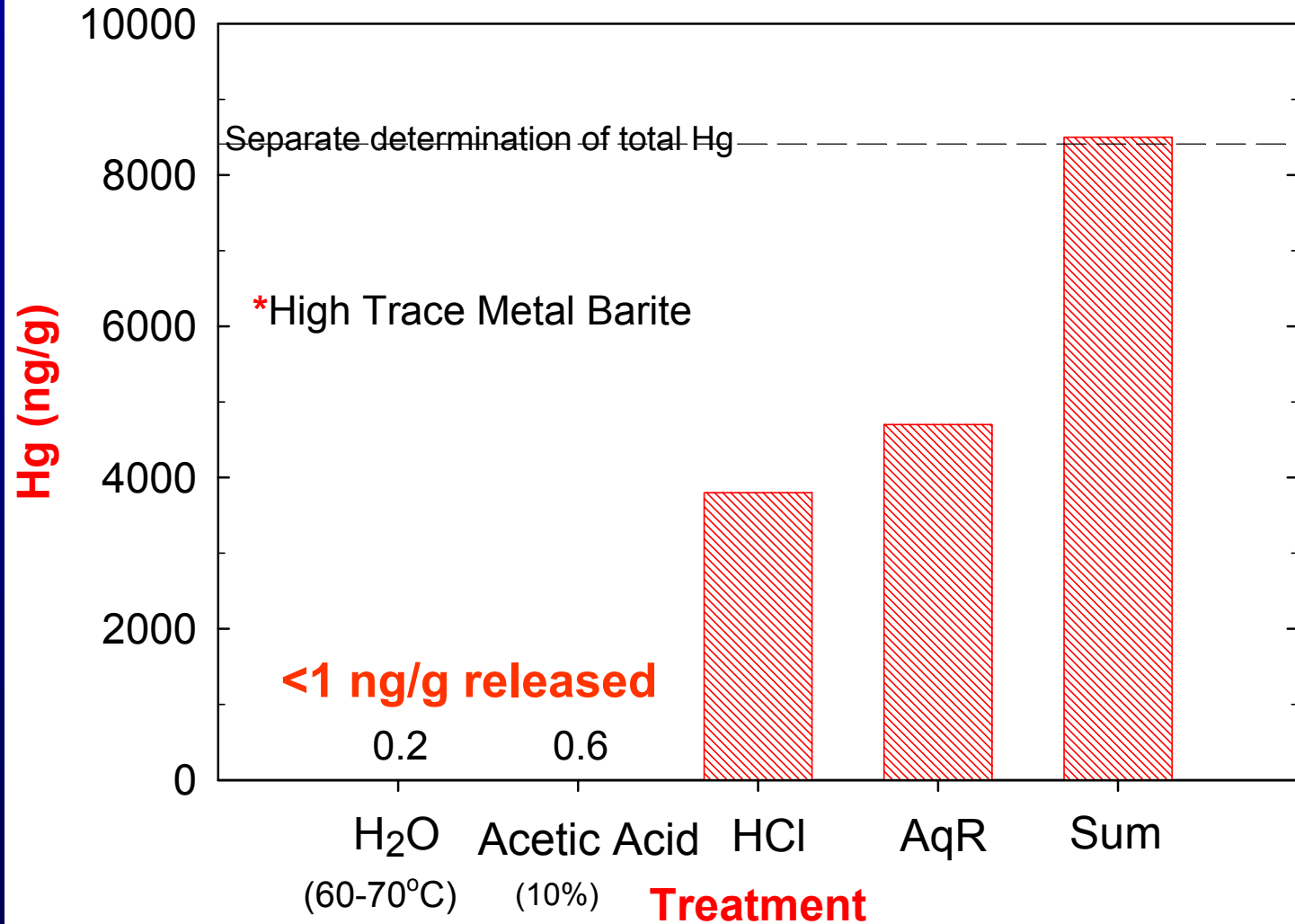


Barite -  
Pyrite-  
Sphaelerite



Massive  
Pyrite

# Sequential Chemical Leaching of Barite\* for Hg



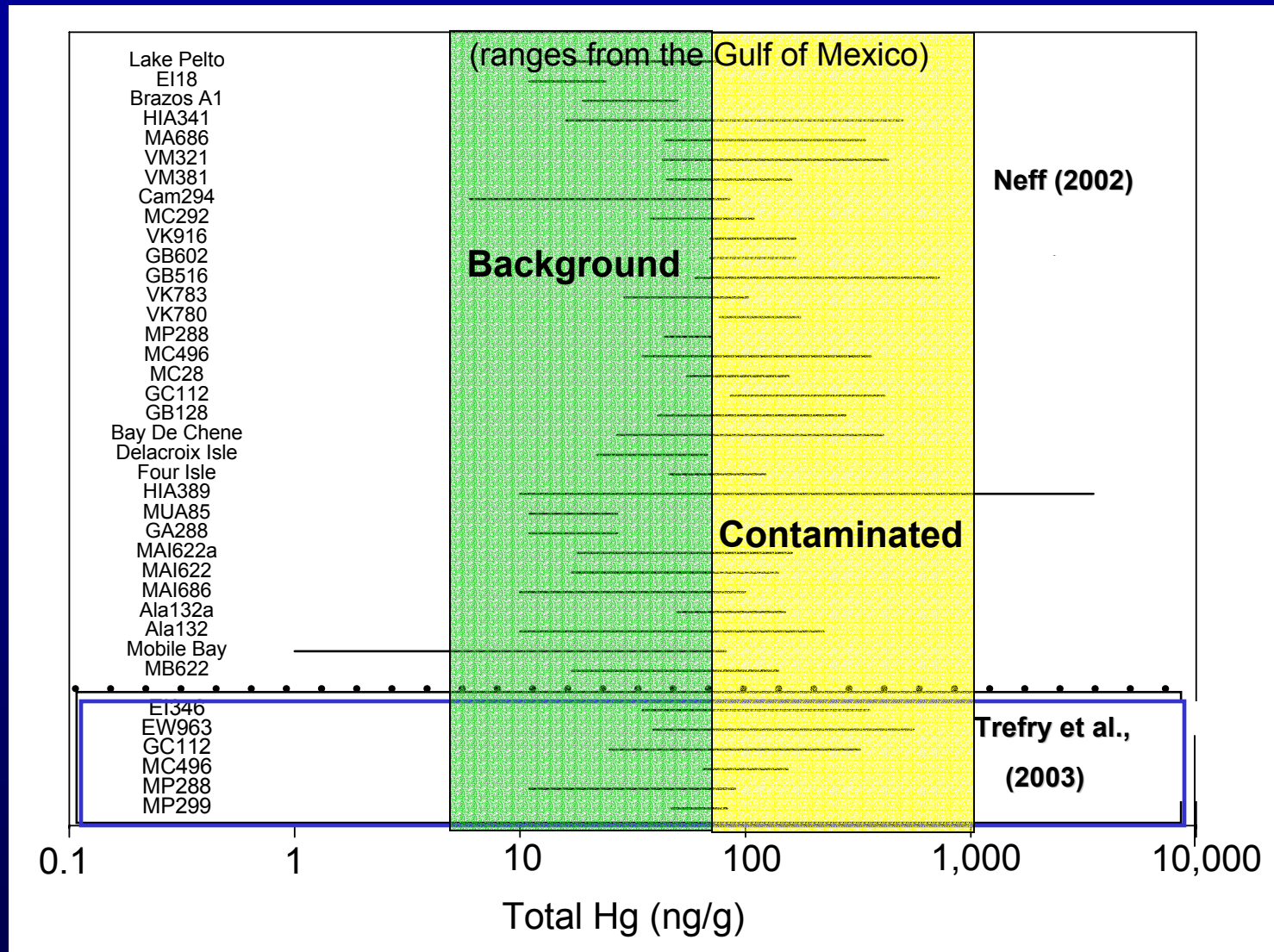
**<0.1% of the total Ba ( $\Sigma = 535,000 \mu\text{g/g}$ )  
was leached with the four treatments.**

# pH leaching of barite for Hg release

at pH 2, 3, 4, 5 and 6

<2 ng Hg/g barite was leached, or  
<0.02% of total Hg in barite with  
8,400 ng/g.

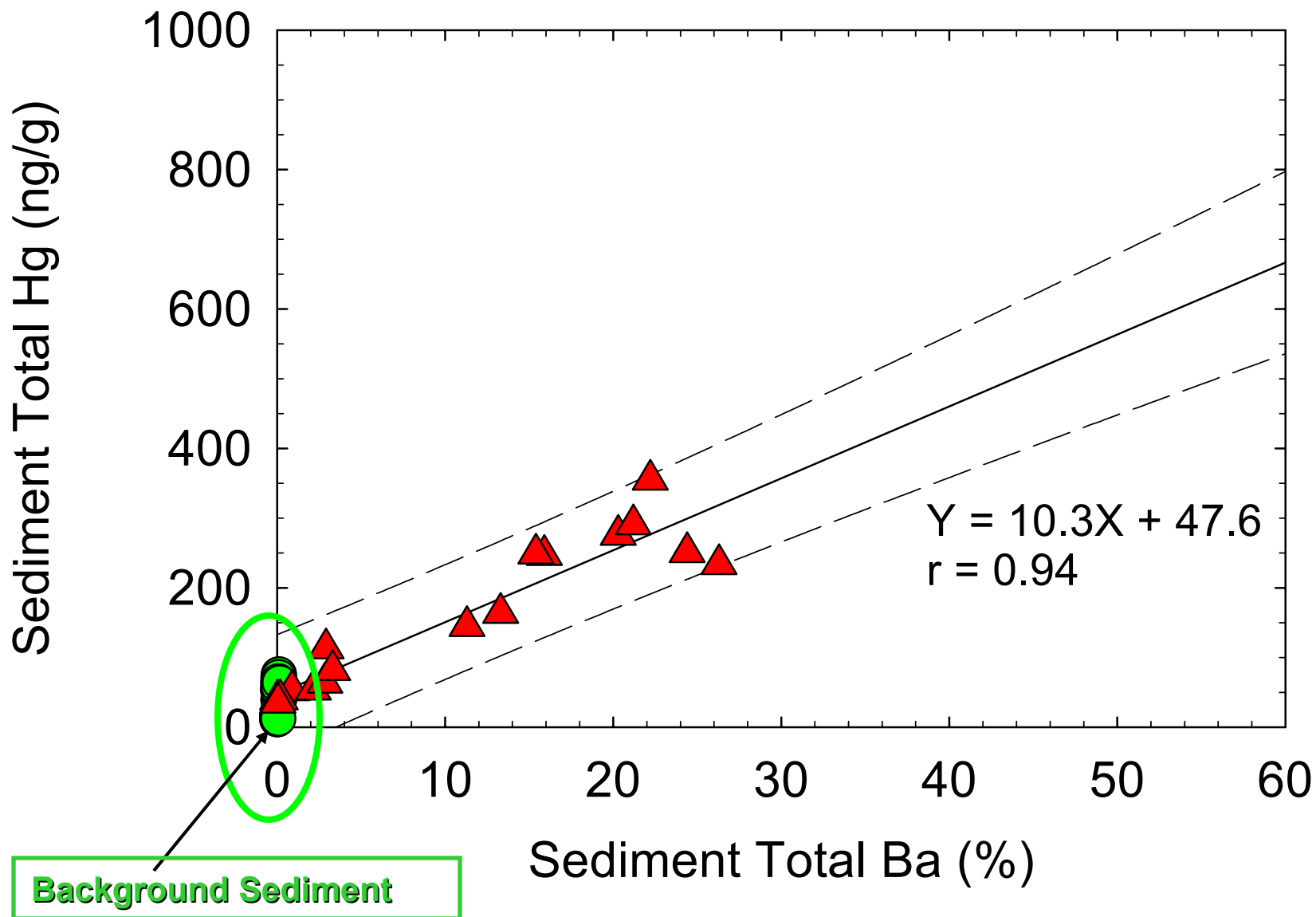
# Total Hg in Sediment Near Drill Sites



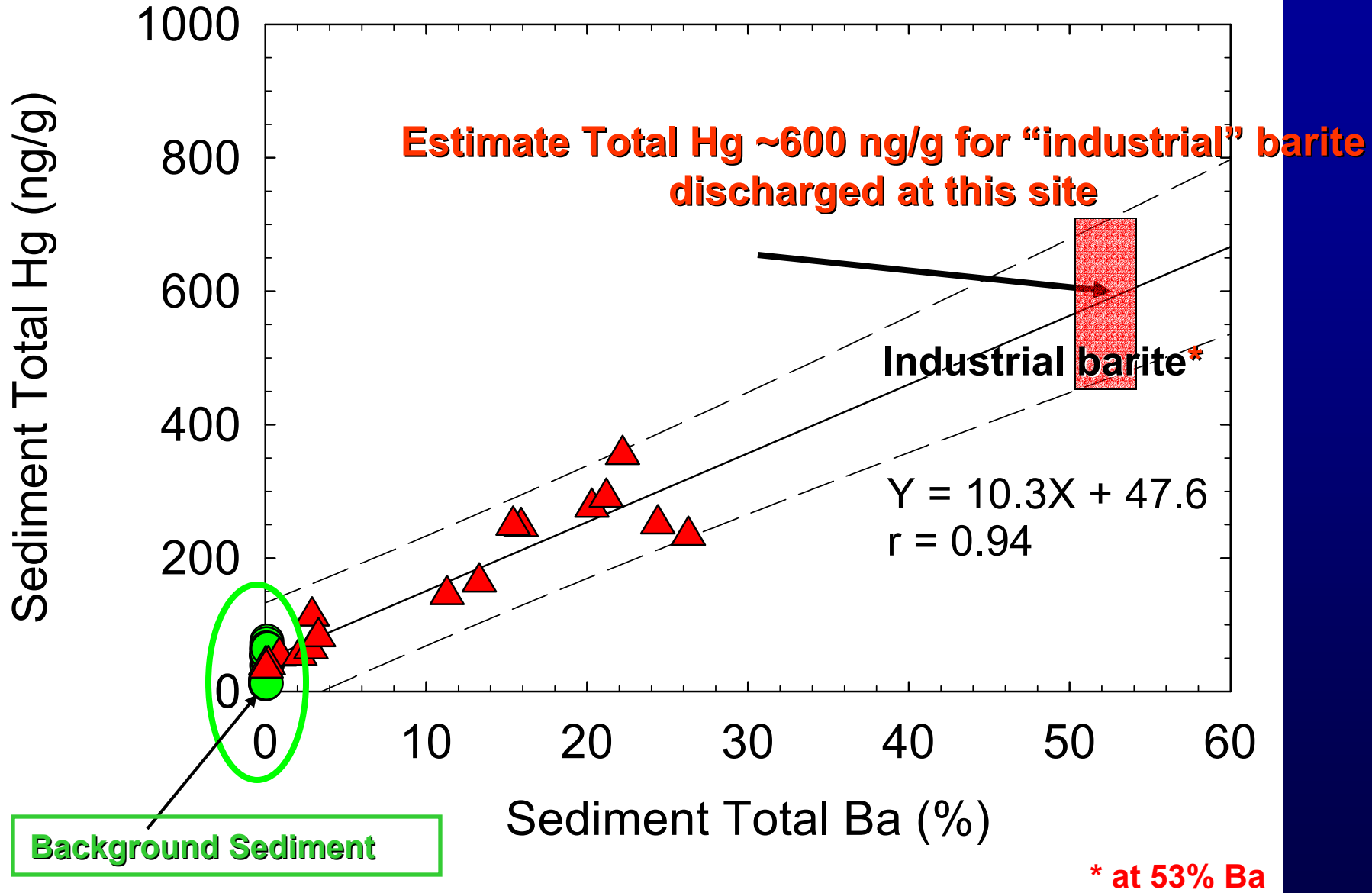
**Concentrations of total Hg in sediment within 100-150 m of drill sites are often 2-20 times more than background levels.**

*\* Lower limit uncertain < or ND levels reported*

**Sediment collected <100 m from drill site in Gulf of Mexico**

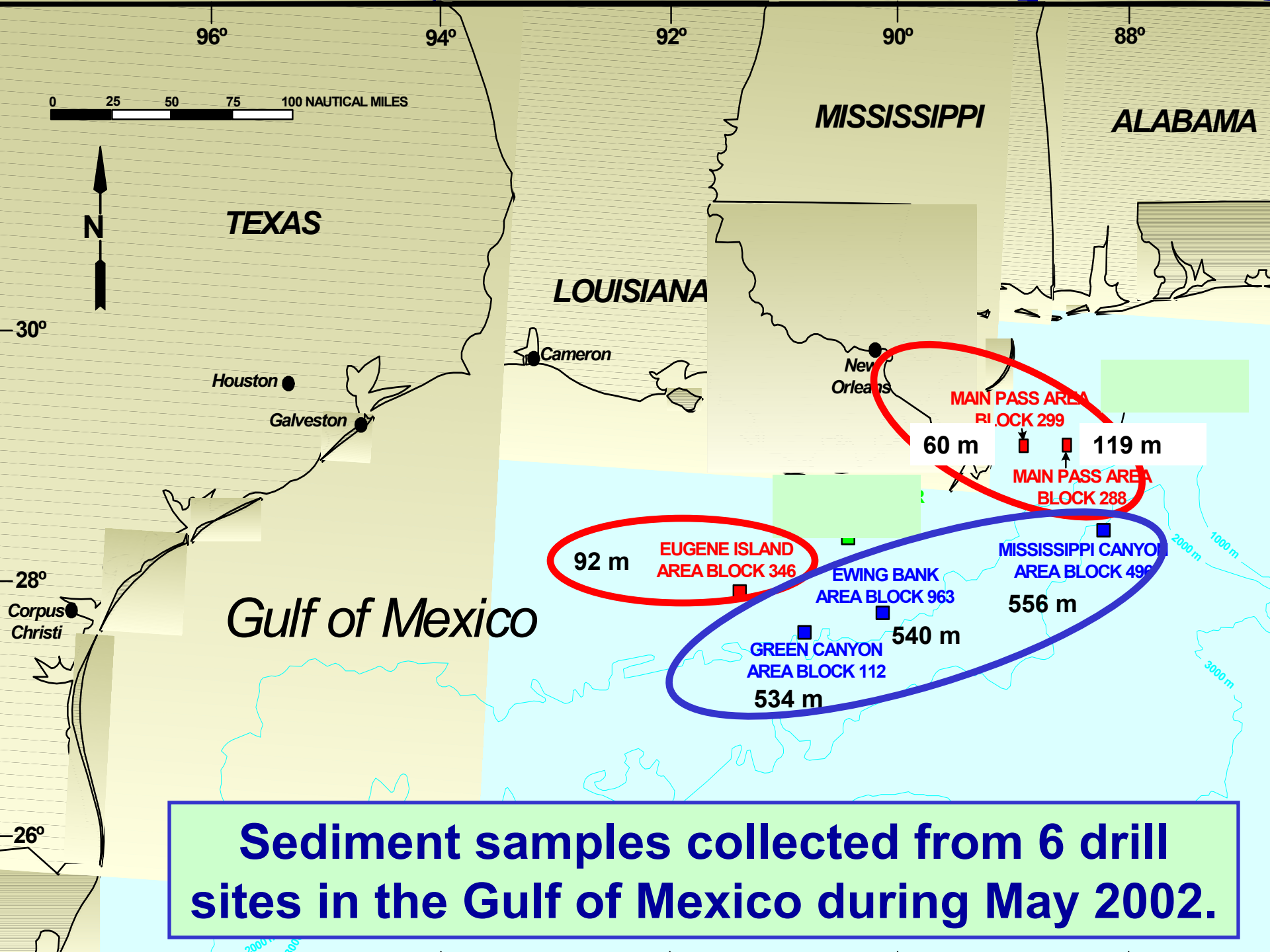


**EPA regulates Hg at 1000 ng/g (ppb) in barite.**



**To what degree does excess total Hg in sediment around offshore drilling sites become MeHg?**





**Sediment samples collected from 6 drill sites in the Gulf of Mexico during May 2002.**

# Total Hg in sediment

Mean  $\pm$  Std Dev

Range

---

**FF\*** (n = 62) **60  $\pm$  21 ng/g**

**11 - 92 ng/g**  
(sand) (clay)

**NF\*\*** (n = 109) **115  $\pm$  94 ng/g**

**25 - 558 ng/g**

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**Total Hg levels significantly higher @ NF sites  
for 5 of 6 drill sites (t-test,  $\alpha = 0.05$ , two-  
tailed).**

\*FF = Farfield @ >3000 m from drill site.

\*\*NF = Nearfield @ <100 m from drill site.

# MeHg in sediment

Mean  $\pm$  Std Dev

---

**NF** (n=109) **0.45  $\pm$  0.41** ng/g

**FF** (n = 62) **0.44  $\pm$  0.27** ng/g

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# MeHg in sediment

Mean  $\pm$  Std Dev

Range

---

<b>NF</b> (n=109)	<b>0.45 <math>\pm</math> 0.41 ng/g</b>	<b>&lt;0.03 – 2.7 ng/g</b>
<b>FF</b> (n = 62)	<b>0.44 <math>\pm</math> 0.27 ng/g</b>	<b>0.2 – 1.1 ng/g</b>

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abundant H<sub>2</sub>S present, stay tuned.

# MeHg in sediment

Mean  $\pm$  Std Dev

Range

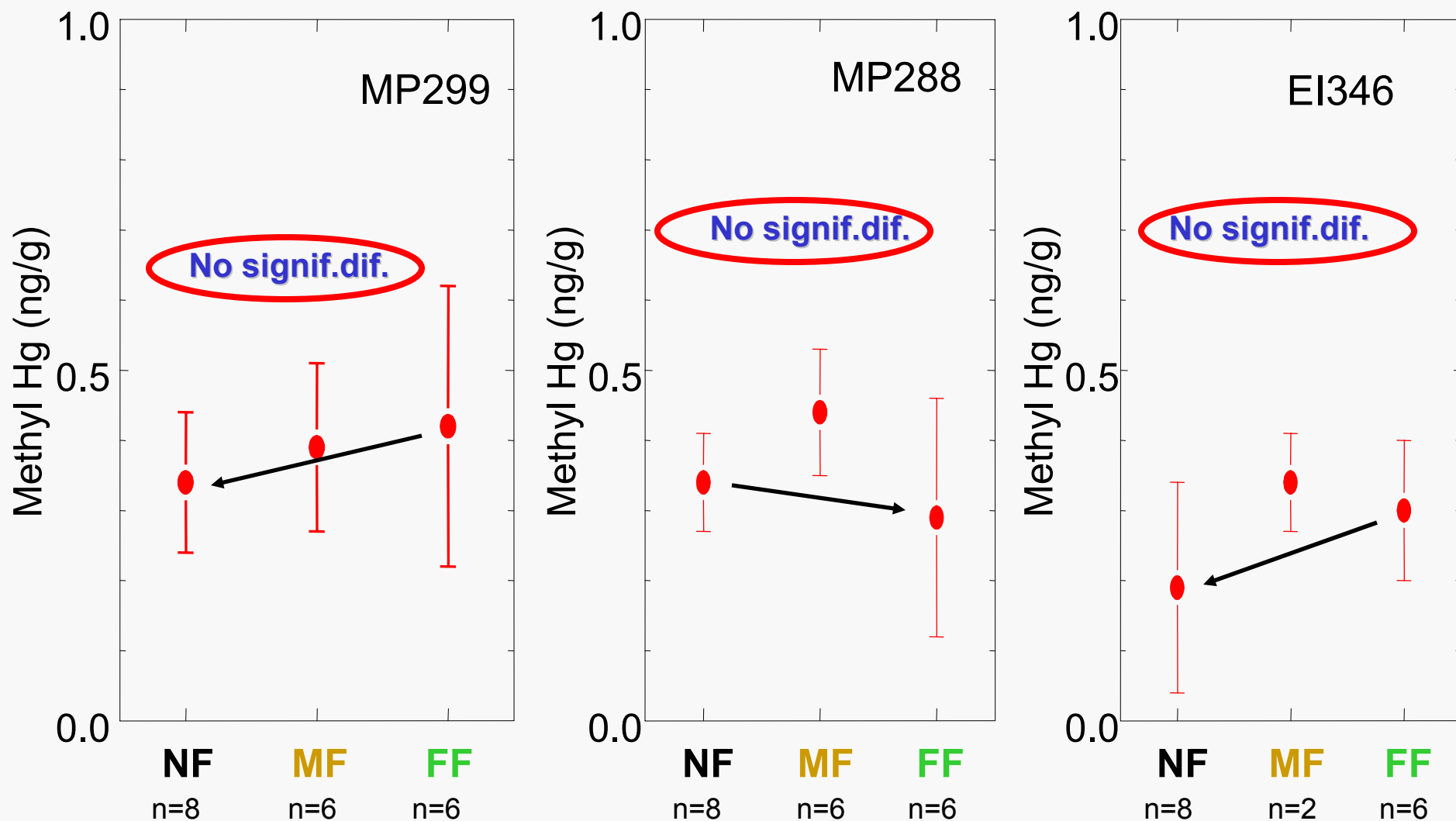
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<b>NF</b> (n=109)	<b>0.45 <math>\pm</math> 0.41 ng/g</b>	<b>&lt;0.03 – 2.7 ng/g</b>
<b>FF</b> (n = 62)	<b>0.44 <math>\pm</math> 0.27 ng/g</b>	<b>0.2 – 1.1 ng/g</b>

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**MeHg levels in surface sediment are not significantly different between NF and FF sites for 6 drilling sites studied**  
(t-test,  $\alpha = 0.05$ , two-tailed).

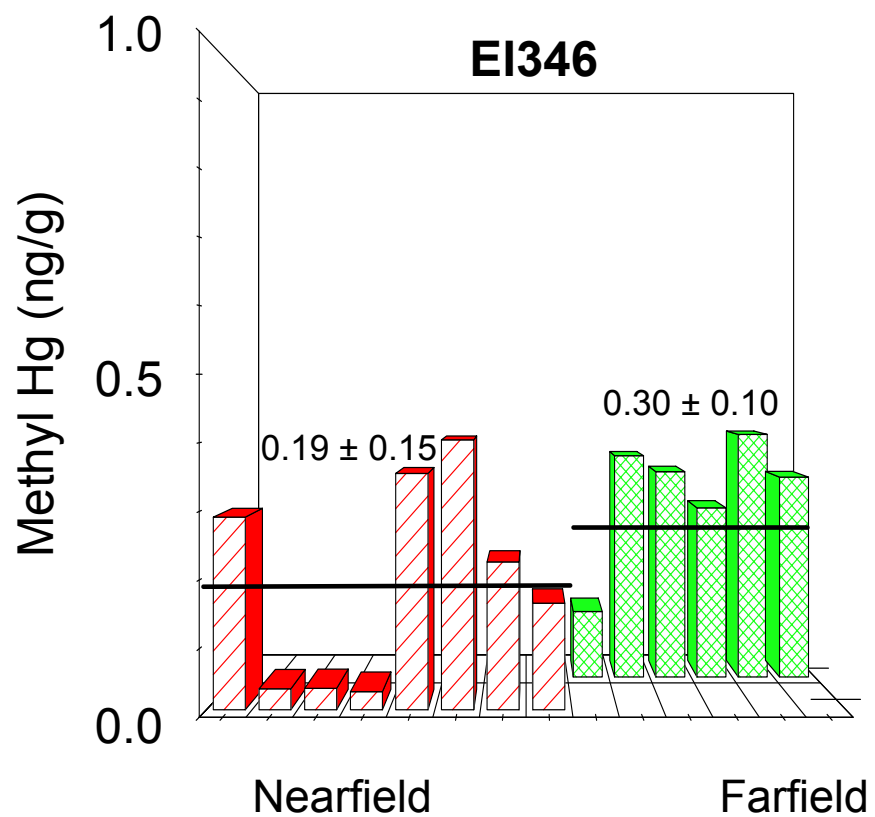
# Shelf Sediment - MeHg - Surface (0-2 cm)



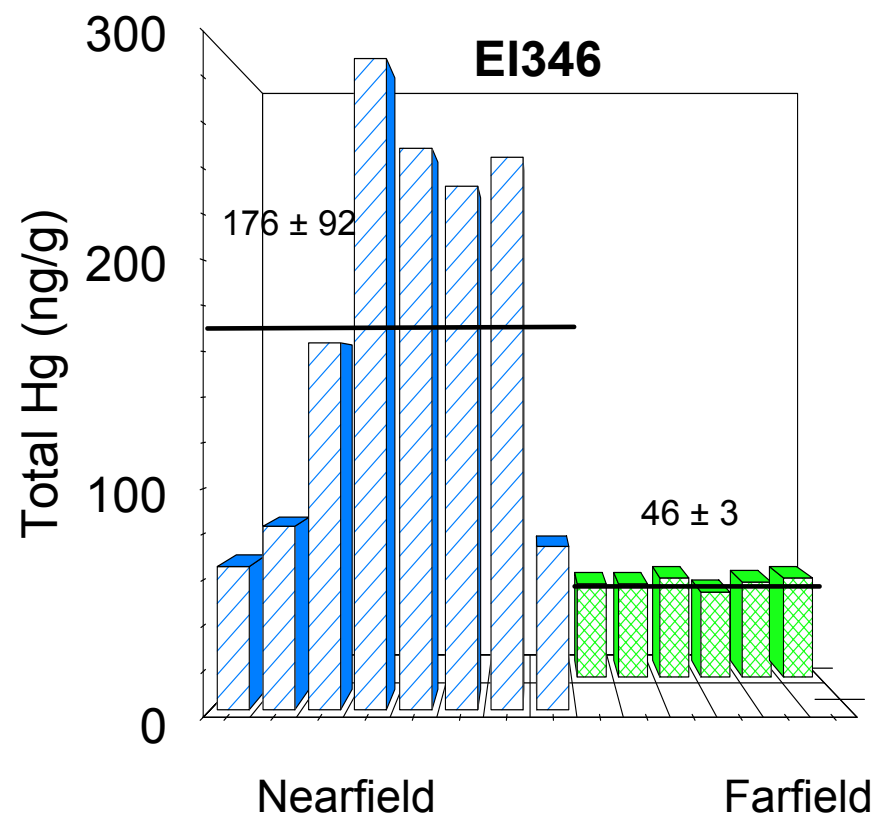
\* (t-test,  $\alpha = 0.05$ , two-tailed).

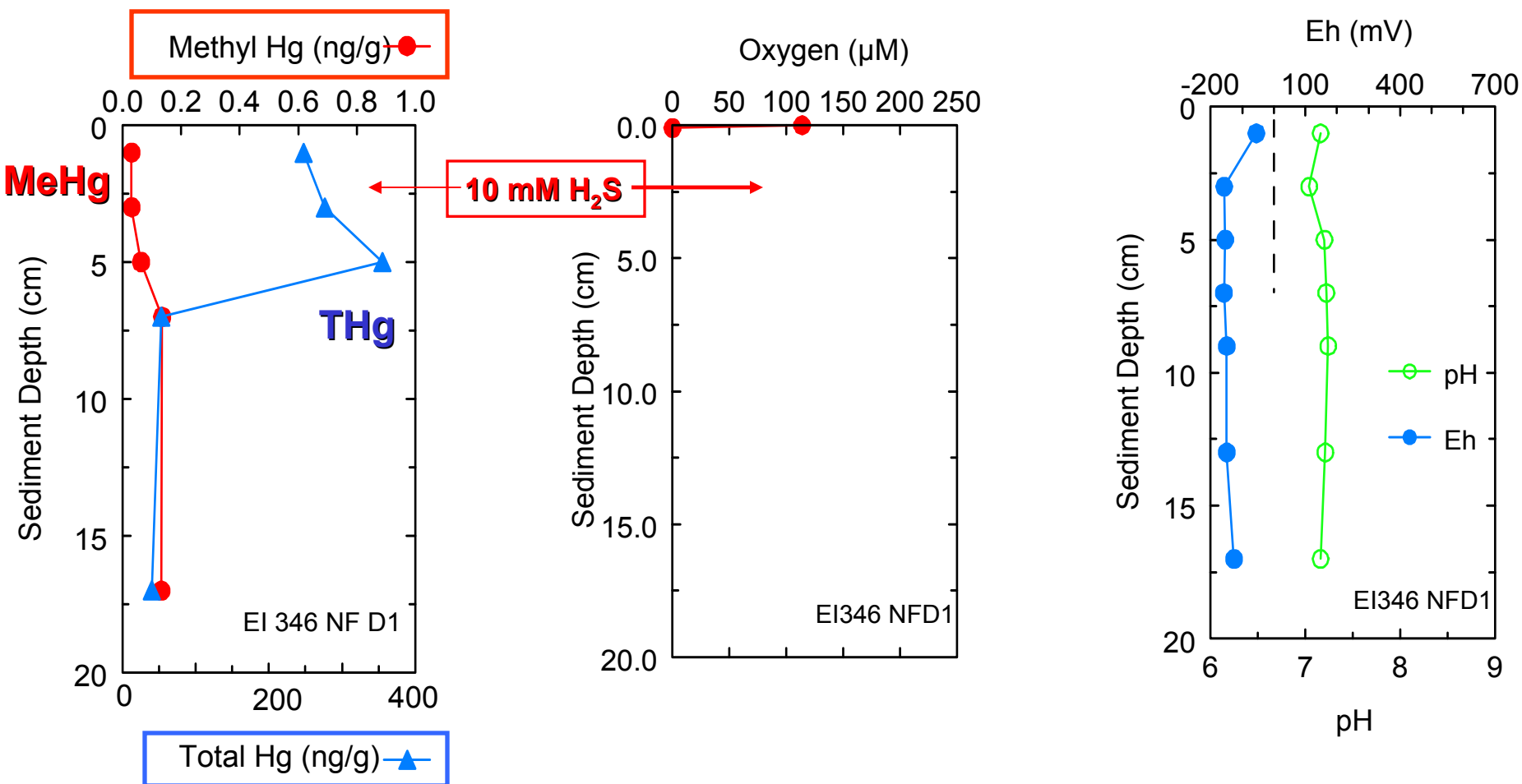
NF = near-field (<100 m); MF = mid-field (100-250 m); FF = far-field (>3000 m)

## MeHg



## Total Hg





In the presence of high levels of H<sub>2</sub>S, MeHg was not detected.

# Total Hg (ng/g, dry wt.) in biota

Laboratory Exposure for 13 weeks to sediment containing barite.

Species	Control	LTMB <sup>1</sup>	HTMB <sup>2</sup>
Sediment	20	120	15,000
Flounder ( <i>Pleuronectes americanus</i> )	240	230	210
Clams ( <i>Mya arenaria</i> )	170	<u>300*</u>	<u>690*</u>

\*Significantly higher than control.

<sup>1</sup>Low Trace Metal Barite

<sup>2</sup>High Trace Metal Barite

(Neff et al., 1989)

# Total Hg (ng/g, dry wt.) in biota

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Clams ( <i>Mya arenaria</i> )	170	<u>300*</u>	<u>690*</u>
Sand Worm ( <i>Neanthes virens</i> )	100	100	150
Grass Shrimp ( <i>Palaemonetes pugio</i> )	150	<u>350*</u>	270

\*Significantly higher than control.

<sup>1</sup>Low Trace Metal Barite

<sup>2</sup>High Trace Metal Barite

(Neff et al., 1989)

# Produced Water – formation water associated with petroleum deposit.

Total Hg in produced water  
<10 – 200 ng/L

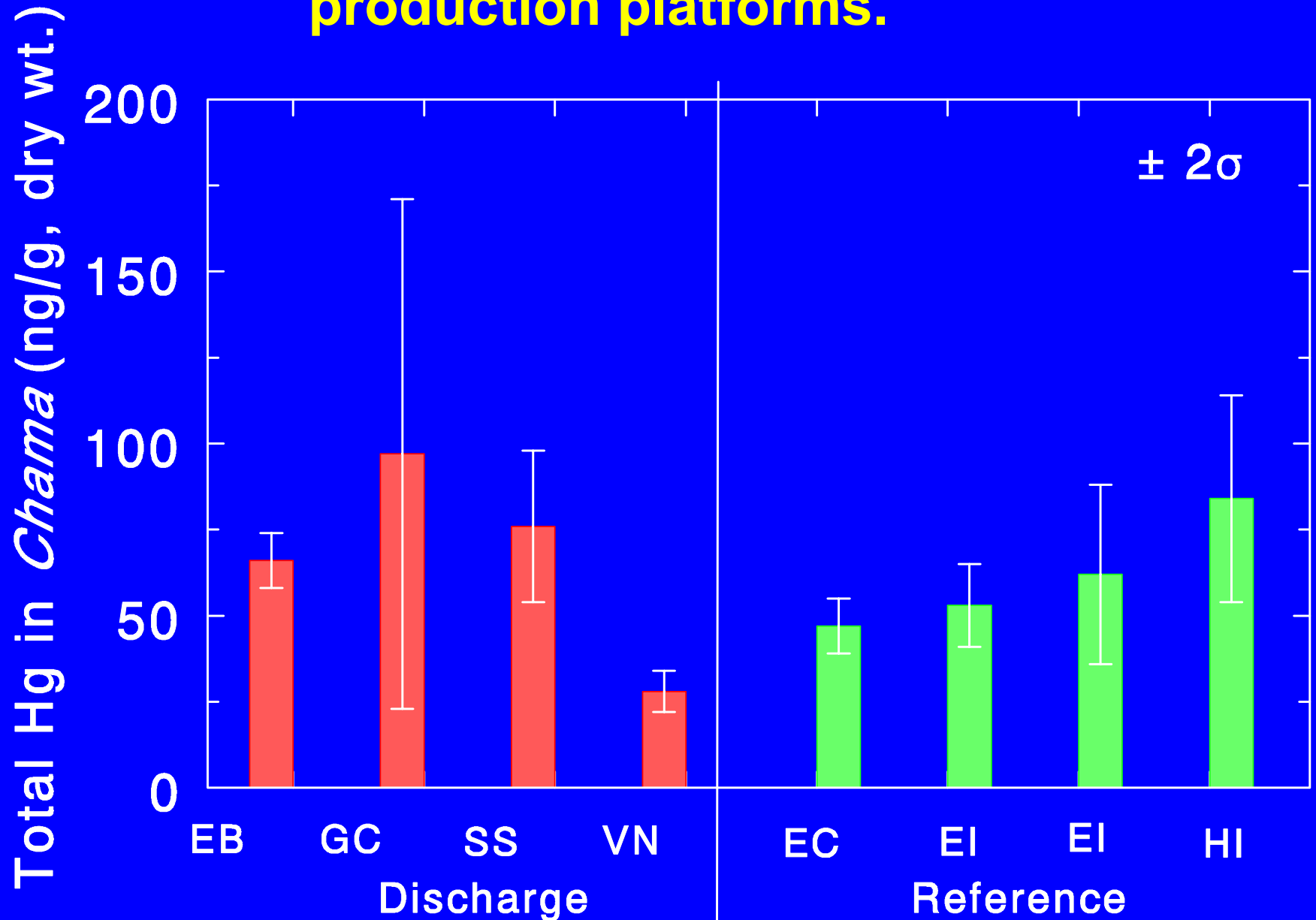
Total Hg in seawater  
Gulf of Mexico  
0.5 – 1.5 ng/L



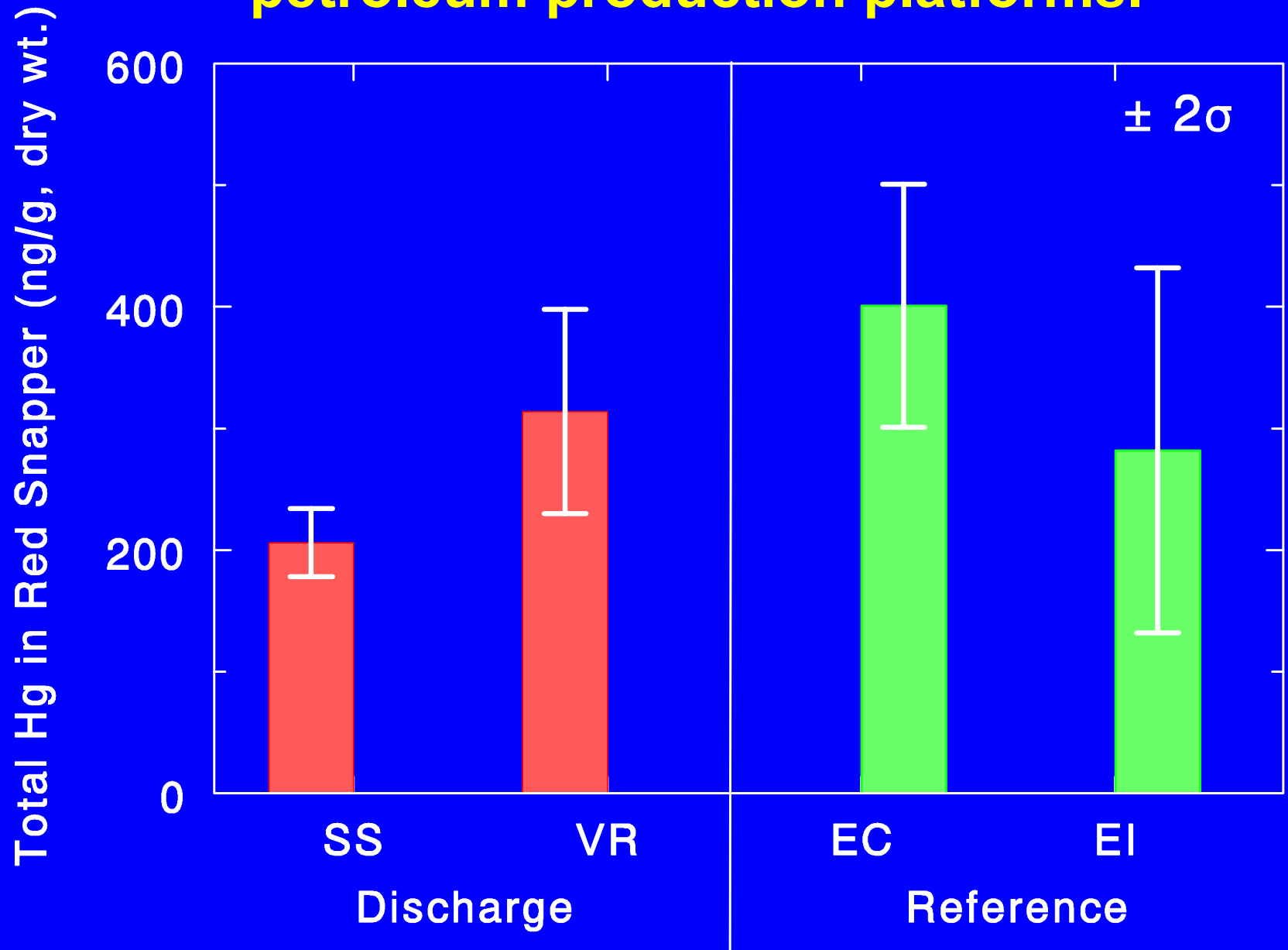
**Hg in mussels** (*Mytilus edulis*) deployed for 1 month in cages near oil production platforms in the North Sea. (Roe Utvik et al., 2002)

Distance from Platform	Hg (ng/g)
0.5 km	18
0.5 km	18
0.5 km	16
1 km	15
10 km	18
10 km	18
15 km	16
>20 km	16

# Hg in oysters collected from petroleum production platforms.



# Hg in red snapper fish collected under petroleum production platforms.



# Overview of Sources

Source	kg Hg/yr
<b>Drilling Fluids</b>	
<b>Produced Water</b>	
<b>Miss. R. particles</b>	
<b>Miss. R. dissolved</b>	
<b>Atmosphere</b>	

## Drilling Fluid inputs to Gulf of Mexico

$(300 \mu\text{g Hg/kg}) \times (1000 \text{ wells/yr}) \times 10^6 \text{ kg/well}$

$= 300 \times 10^9 \mu\text{g Hg/yr} = \underline{300 \text{ kg Hg/yr}}$

# Overview of Sources

Source	kg Hg/yr
<b>Drilling Fluids</b>	<b>300</b>
<b>Produced Water</b>	
<b>Miss. R. particles</b>	
<b>Miss. R. dissolved</b>	
<b>Atmosphere</b>	

## Produced Water inputs to Gulf of Mexico

(<10 to 200 ng Hg/L) x (200 x 10<sup>9</sup> L/yr)

= <2 to 40 kg/yr

# Overview of Sources

Source	kg Hg/yr
<b>Drilling Fluids</b>	<b>300</b>
<b>Produced Water</b>	<b>40</b>
<b>Miss. R. particles</b>	
<b>Miss. R. dissolved</b>	
<b>Atmosphere</b>	

## Mississippi River Particles

$(100 \mu\text{g Hg/kg}) \times (210 \times 10^9 \text{ kg/yr}) =$

**= 21,000 kg particulate Hg/yr**

# Overview of Sources

Source	kg Hg/yr
<b>Drilling Fluids</b>	<b>300</b>
<b>Produced Water</b>	<b>40</b>
<b>Miss. R. particles</b>	<b>21,000</b>
<b>Miss. R. dissolved</b>	
<b>Atmosphere</b>	

## Dissolved

$(3 \text{ ng Hg/L}) \times (4 \times 10^{14} \text{ L/yr}) =$

**= 1,200 kg particulate Hg/yr**

# Overview of Sources

Source	kg Hg/yr
<b>Drilling Fluids</b>	<b>300</b>
<b>Produced Water</b>	<b>40</b>
<b>Miss. R. particles</b>	<b>21,000</b>
<b>Miss. R. dissolved</b>	<b>1,200</b>
<b>Atmosphere</b>	

## Atmospheric Inputs to GOM Shelf

$$(15 \mu\text{g Hg/m}^2) \times (340 \times 10^9 \text{ m}^2)$$

$$= 5,100 \text{ kg Hg/yr}$$

# Overview of Sources

Source	kg Hg/yr
<b>Drilling Fluids</b>	<b>300</b>
<b>Produced Water</b>	<b>40</b>
<b>Miss. R. particles</b>	<b>21,000</b>
<b>Miss. R. dissolved</b>	<b>1,200</b>
<b>Atmosphere</b>	<b>5,100</b>

## Inputs from Drilling Fluids & Produced Water to GOM Shelf

(**300** + **40** kg Hg/yr)

**21,000** + **1,200** + **5,100** kg Hg/yr

≈ **1.2 %** of river and  
atmospheric inputs

# Summary

1. Primary source of Hg in drilling fluids is barite – present as sulfide phase – Hg not easily leached from barite.
2. Concentrations of **Total Hg** significantly greater in NF vs FF sediment at most drilling sites.
3. Concentrations of **MeHg** not significantly different in NF vs FF sediment at 6 drilling sites.
4. Hg inputs to the Gulf of Mexico from drilling fluids and produced water are estimated at 340 kg/yr.

# Conclusions

1. Based on available data, inputs of Hg to the Gulf of Mexico from petroleum drilling fluids and produced water account for ~1% of total Hg inputs to the continental shelf of the GOM.
2. (a) Studies of Hg at various drill sites in shelf and slope waters may provide some potentially useful insights to chemical reactions involving Hg.  
(b) Studies of Hg in benthic biota and pore water at various drill sites may be valuable.
3. Globally, studies of Hg in drilling discharges seem to be a lower priority than studies of other Hg sources.

## Acknowledgements

Bob Trocine (FIT), Minerals Management Service (US DOI, Jim Cimato, Mary Boatman, Margaret Metcalf), Synthetic-Based Muds Working Group (Jim Ray, Joe Smith) Offshore Operators Committee, Eric Crecelius & Jerry Neff (Battelle).



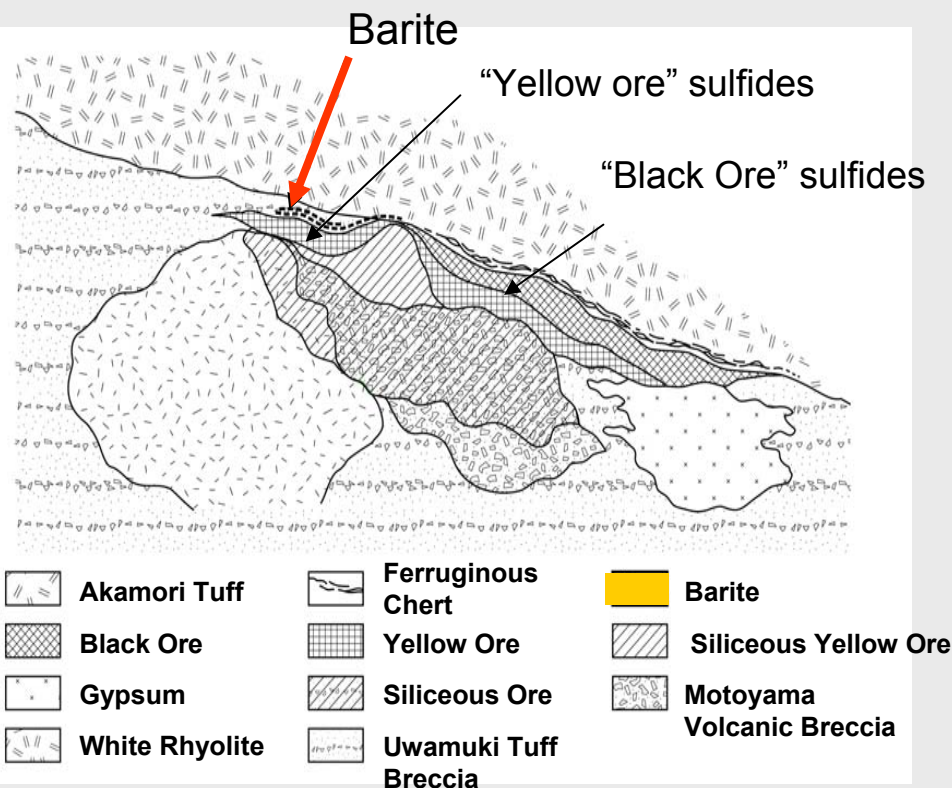
# Extra Slides: Supplement to Presentation



Florida Institute of Technology Drilling Fluids Team

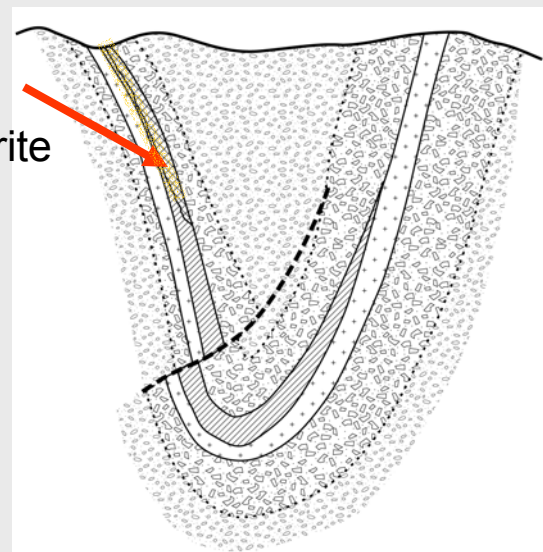
# Barite and Sulfide Minerals in Vein Deposits

## Volcanic/Sedimentary Setting - Japan\*

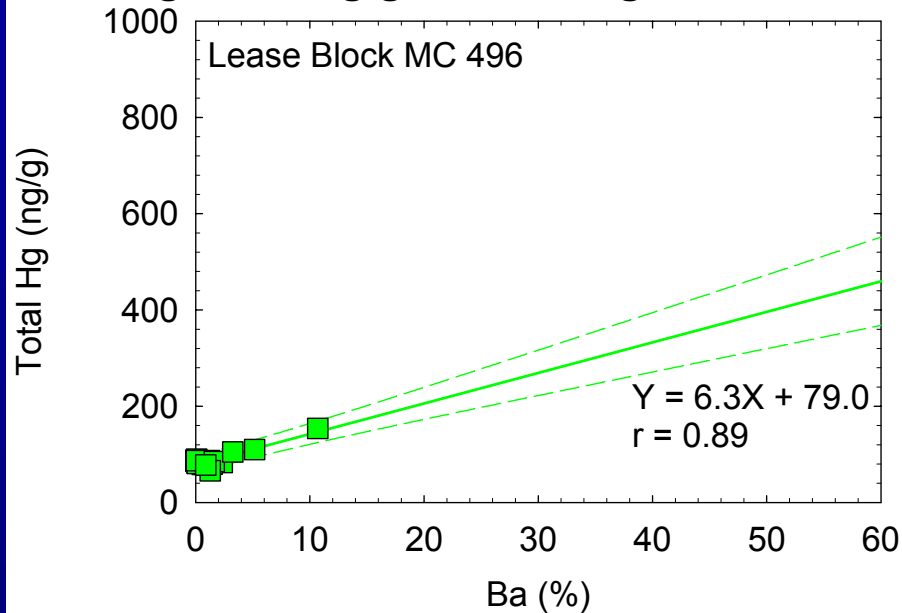


## Metamorphosed Sedimentary Setting - Australia\*\*

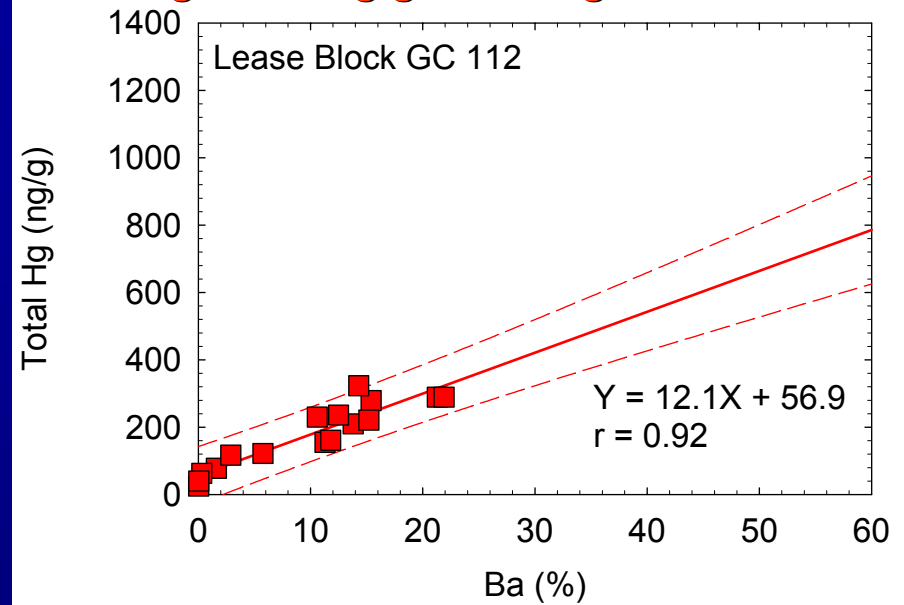
Barite-pyrite-sphalerite ore



**Hg = 410 ng/g in discharged barite.\***

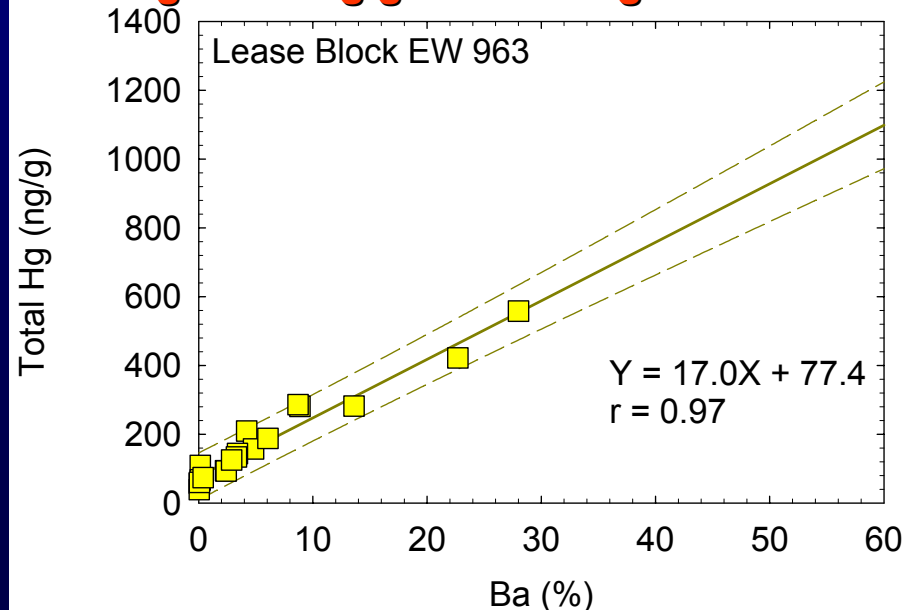


**Hg = 980 ng/g in discharged barite.\***



**Results for  
Gulf of Mexico  
sediment**

**Hg = 700 ng/g in discharged barite.\***



\* at 53% Ba

# Predicting Biological Effects in Sediments

Long et al. (1995)

**Mercury**  
(ng/g)

Background sediment

**10 - 80**

Effects Range Median (ERM)

**710**

Adverse effects

**frequent @ >ERM**

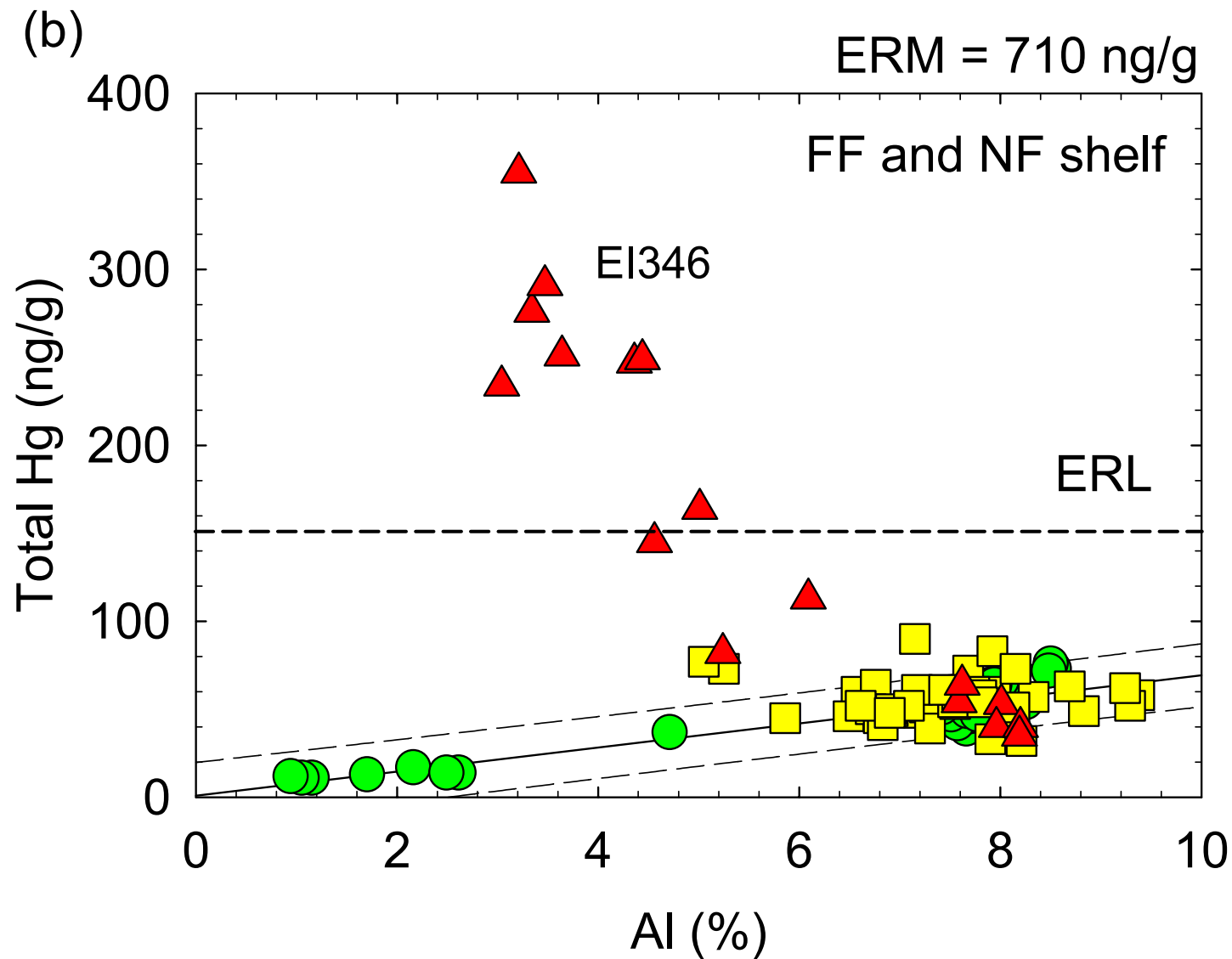
Adverse effects **occasional** between **ERM** and **ERL**.

Effects Range Low (ERL)

**150**

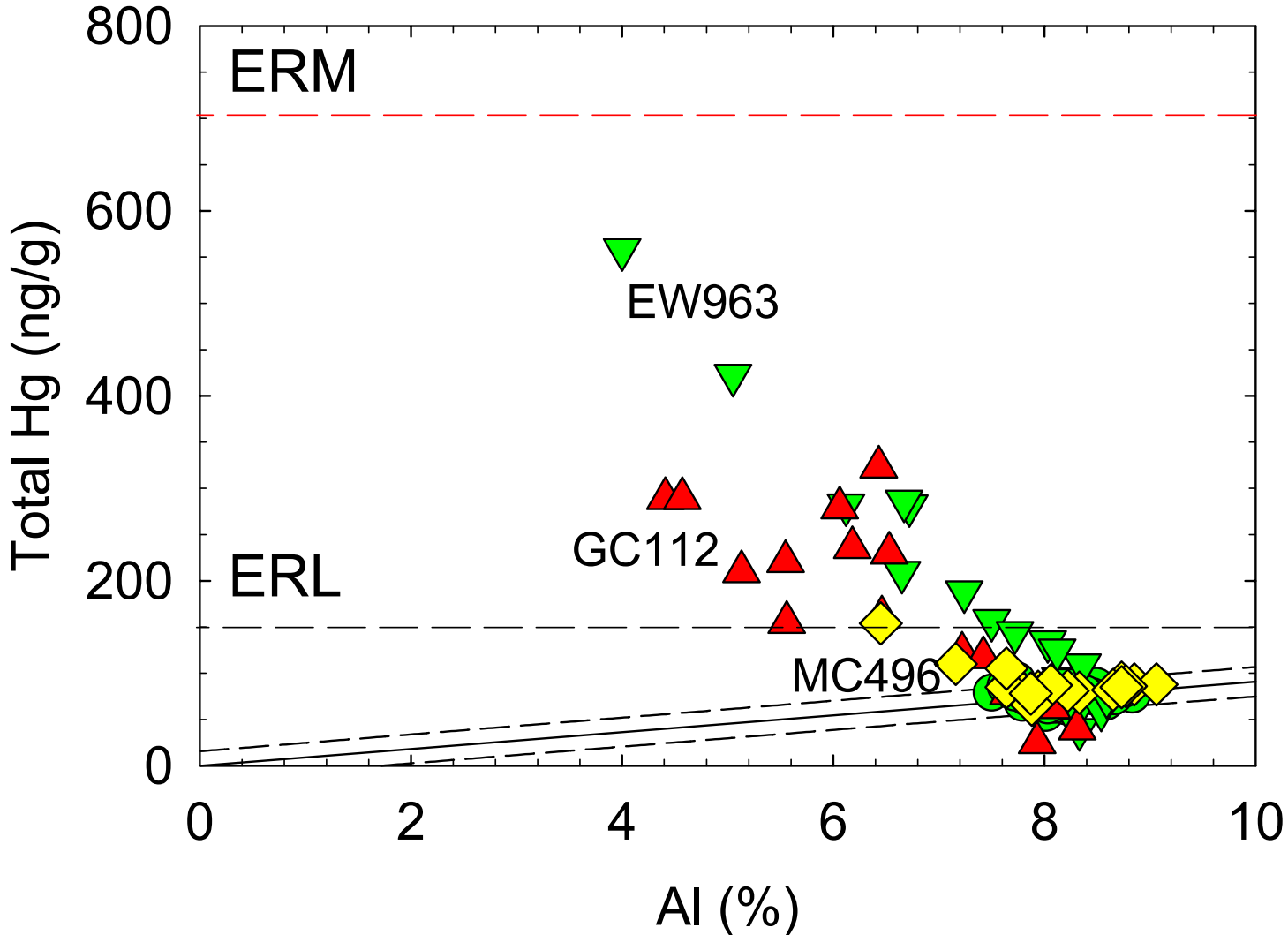
Adverse effects

**rare @ <ERL**

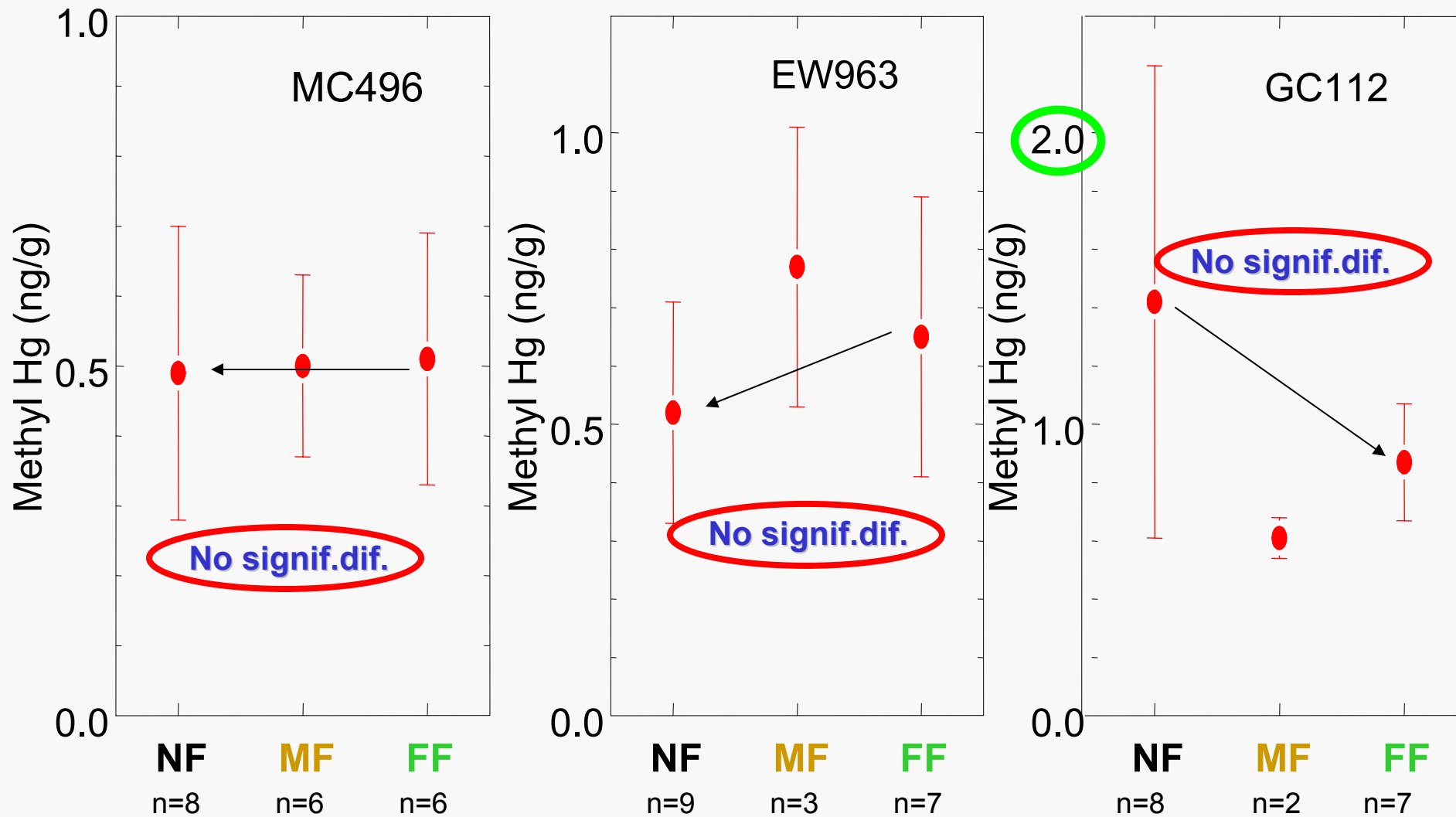


(b)

# FF and NF upper slope

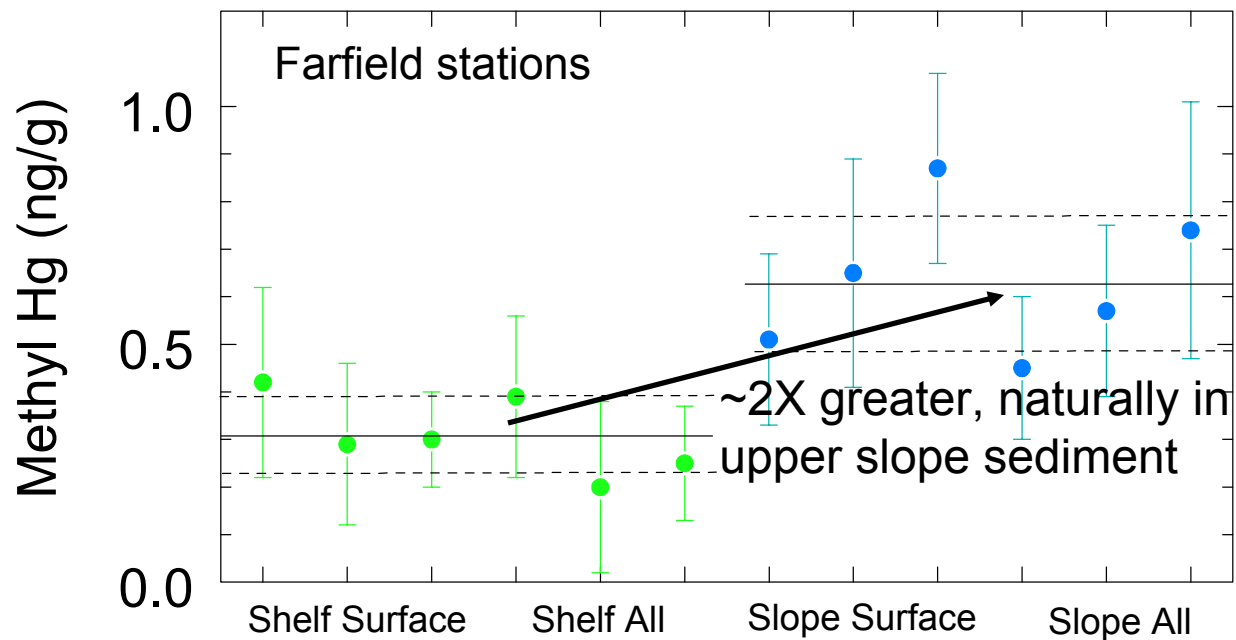


# Upper Slope Sediment - MeHg - Surface (0-2 cm)

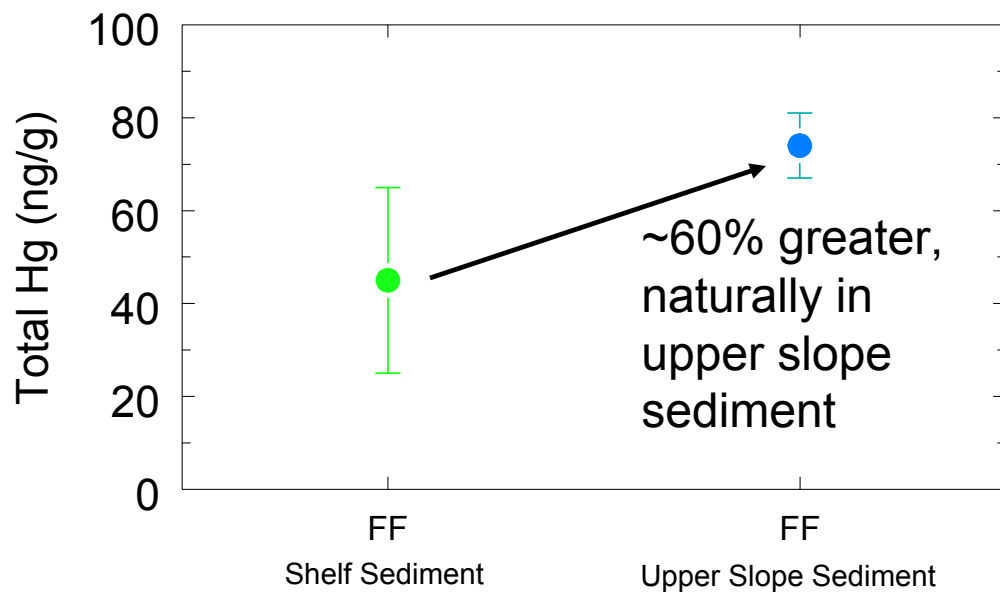


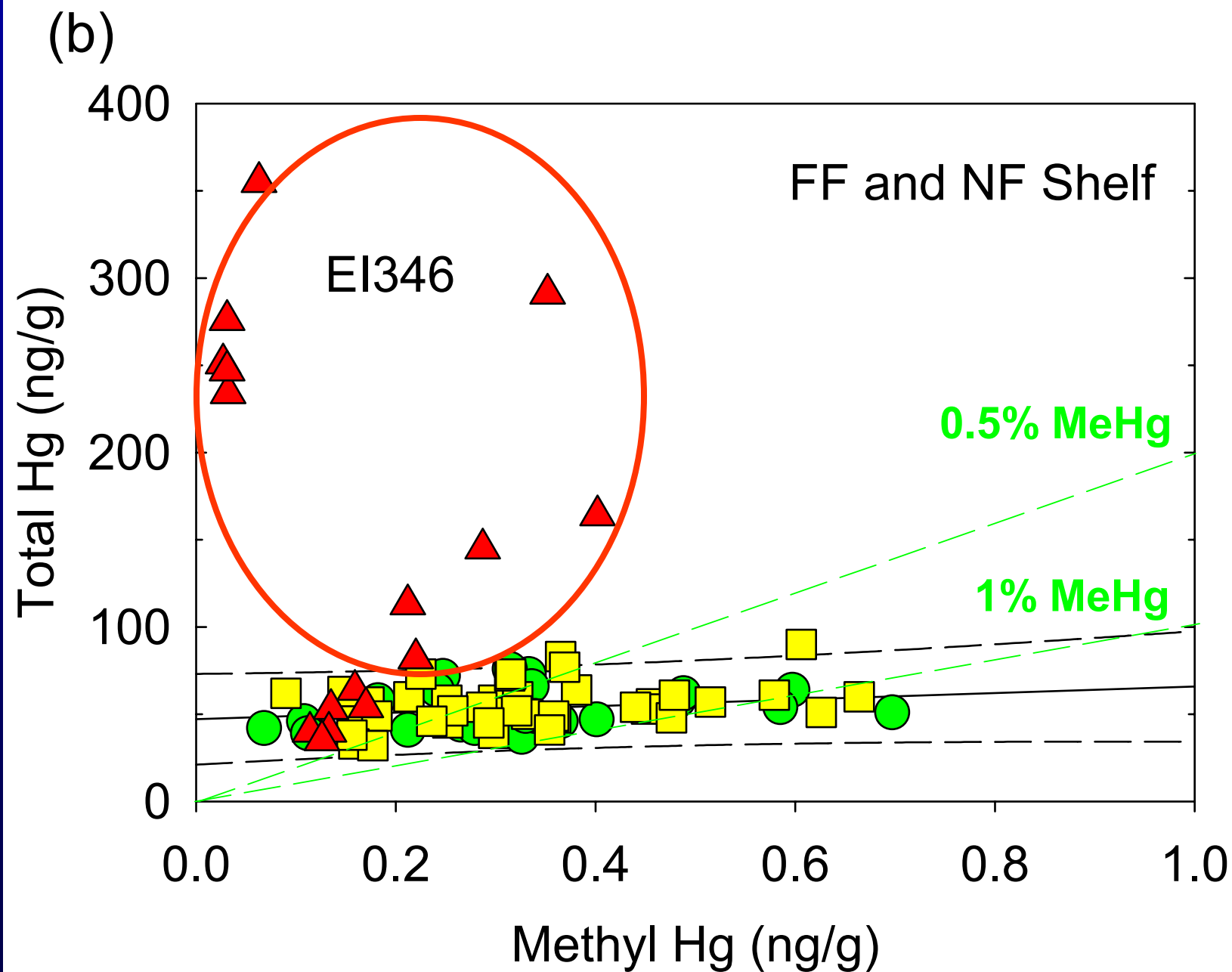
\* (t-test,  $\alpha = 0.05$ , two-tailed).

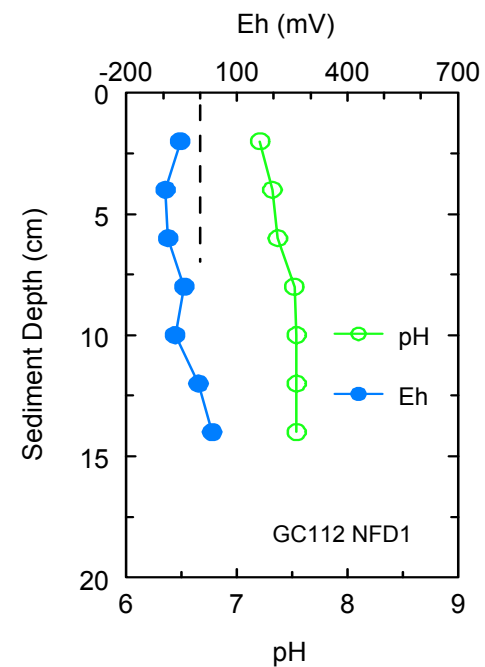
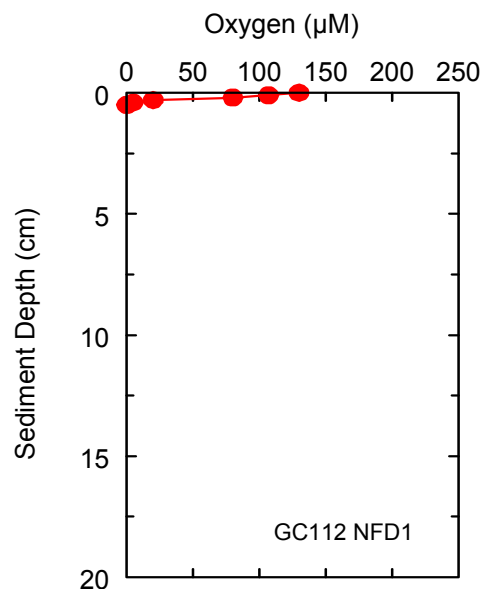
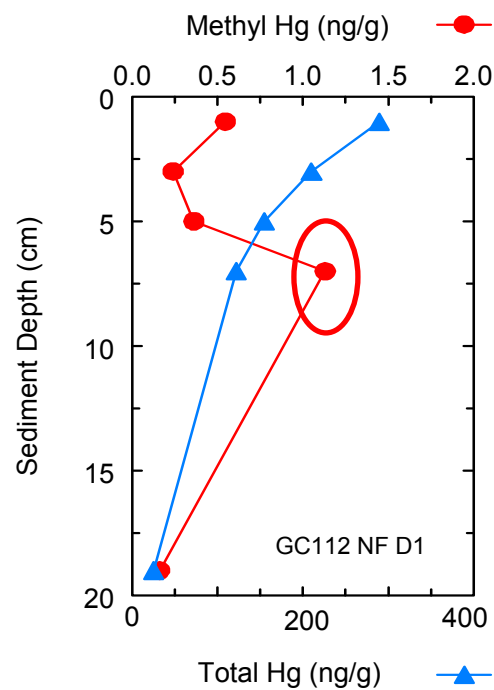
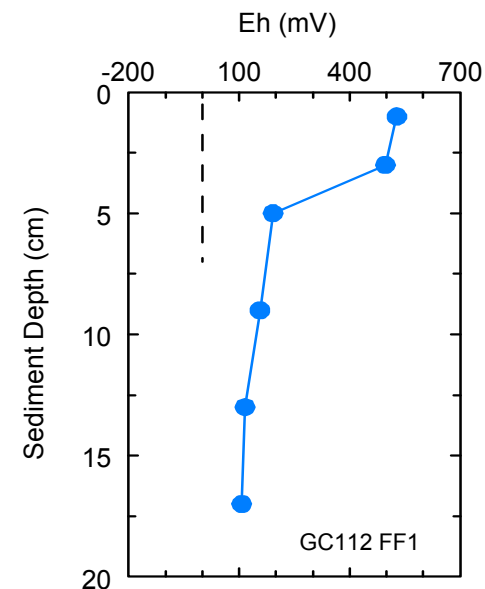
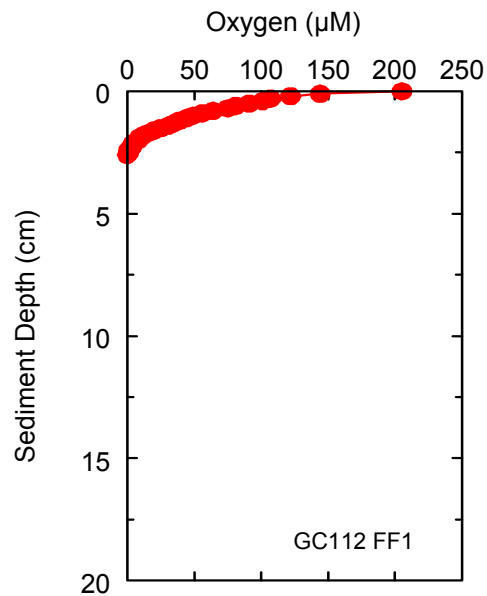
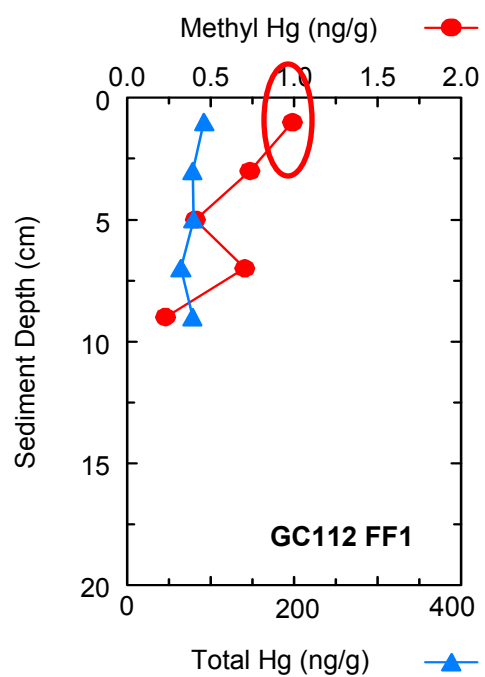
...a natural note.



All background samples





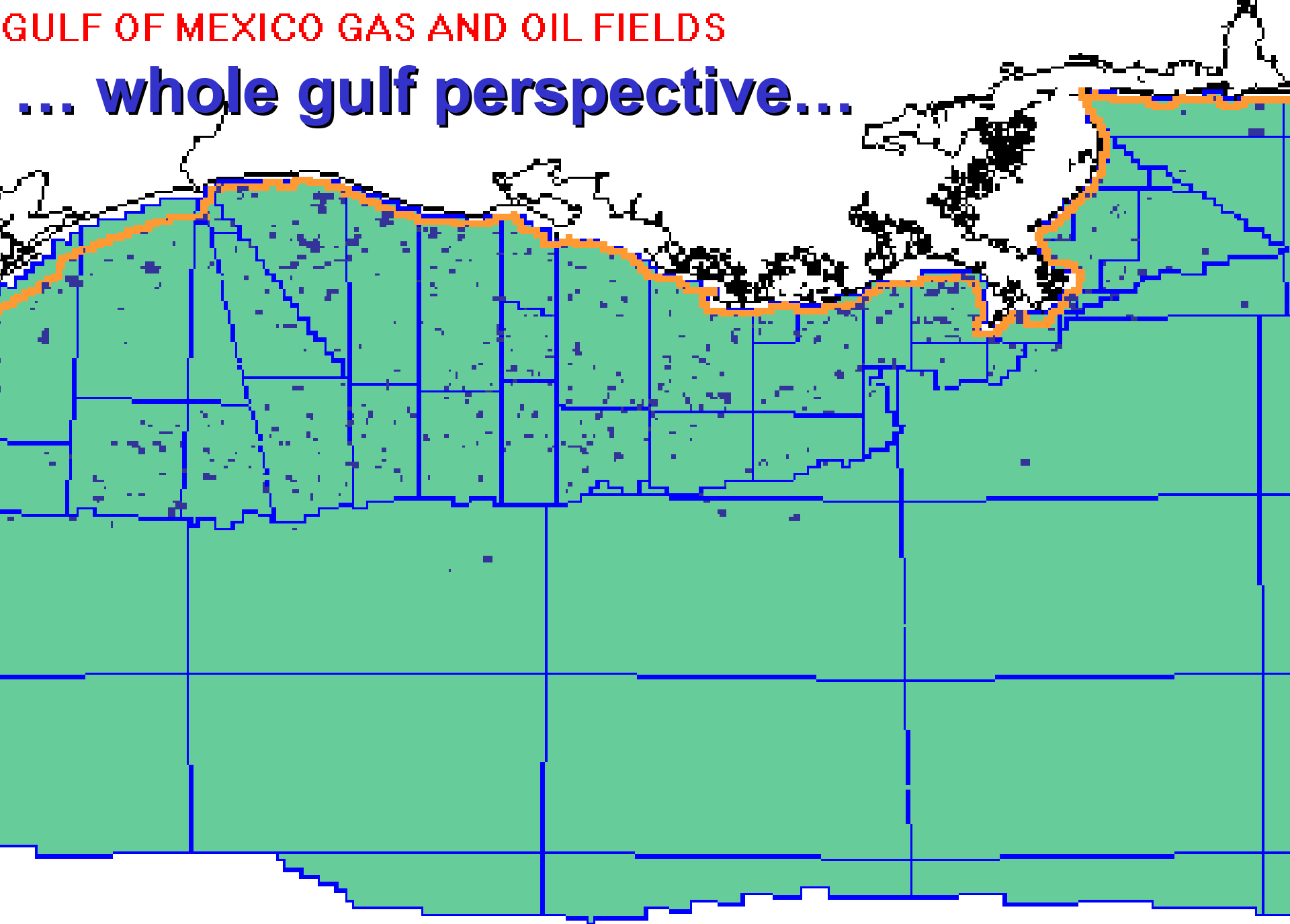


- **MeHg concentrations in sediment appear tied to redoxcline ( $\Delta E_h = -400$  mV)**
- **Formation favored at  $E_h$  of  $0 \pm 100$  mV**
- **Formation less favored in presence of  $H_2S$ ,  $E_h < -100$  mV**

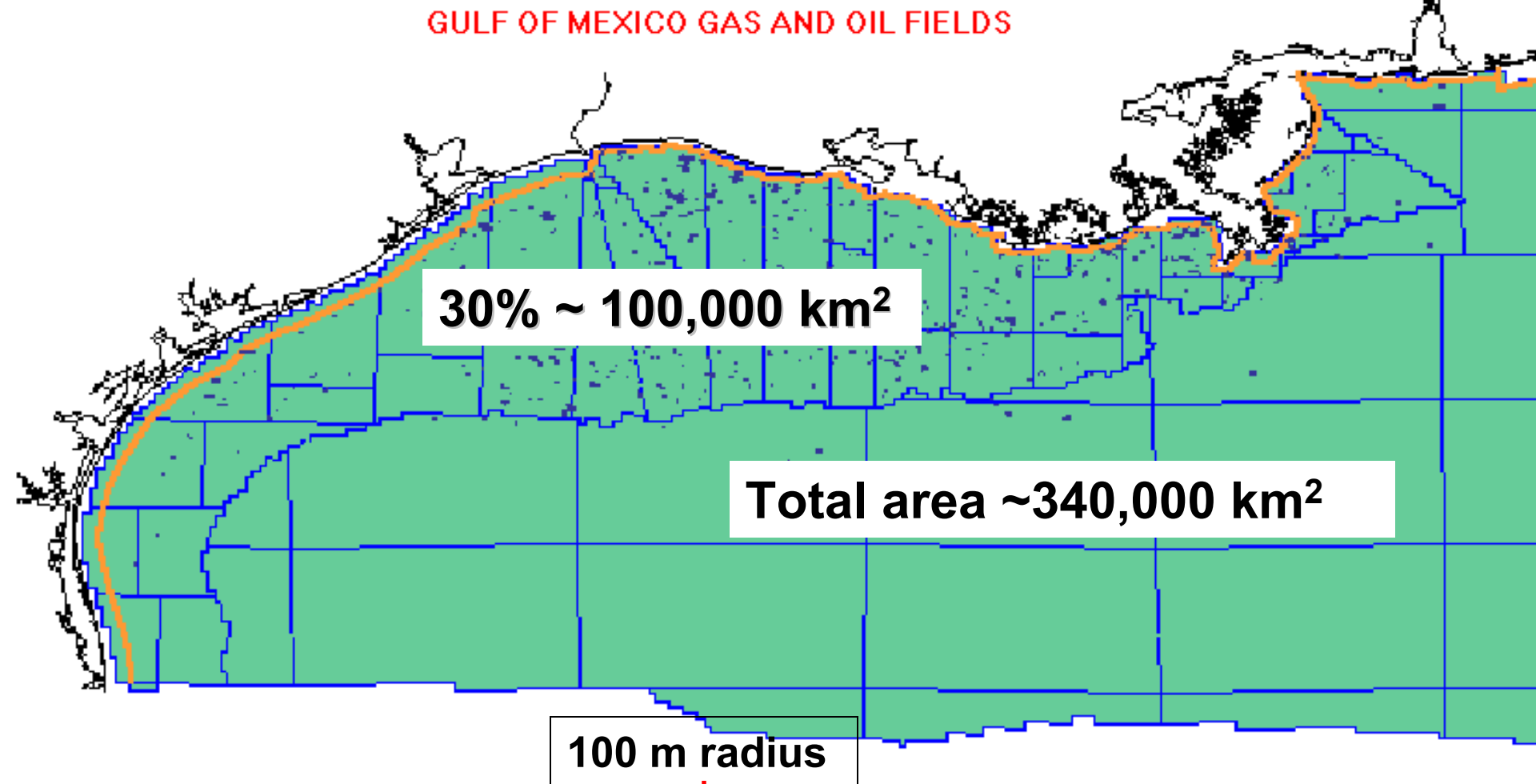
- **Drilling muds can create an environment that limits methylation relative to ambient conditions.**
- **Drilling muds can create an environment that favors methylation relative to ambient conditions.**

# GULF OF MEXICO GAS AND OIL FIELDS

... whole gulf perspective...



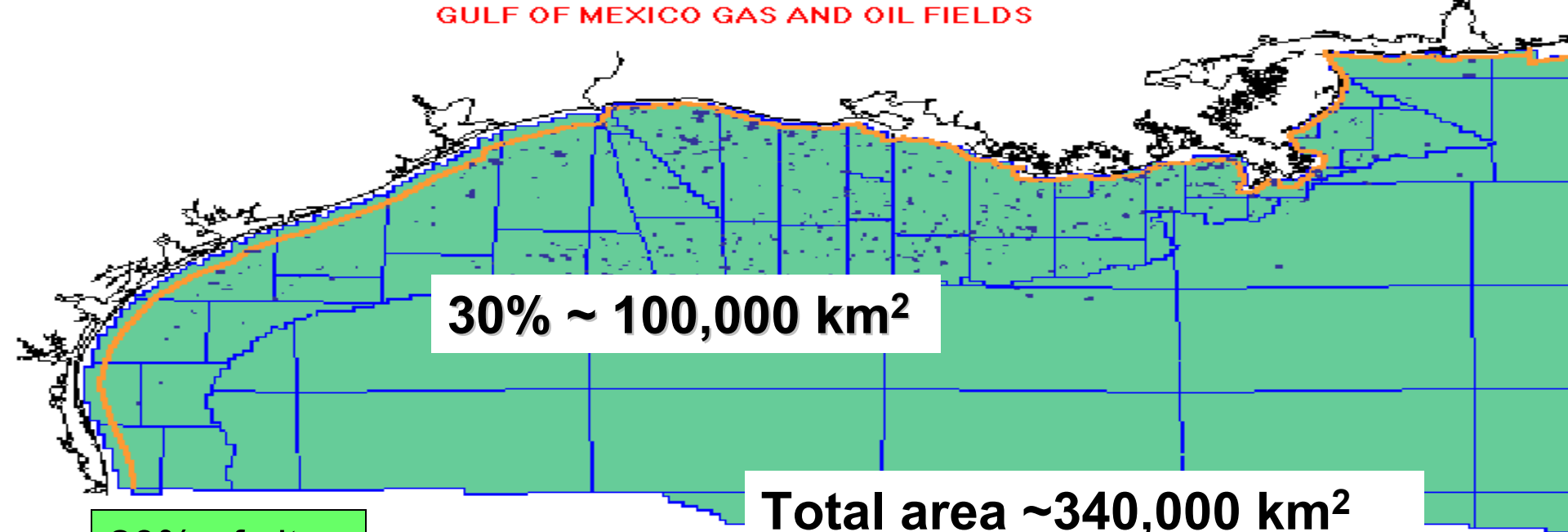
# GULF OF MEXICO GAS AND OIL FIELDS



4000 drilling sites x (0.1 km)<sup>2</sup> x (3.14) ~ 125 km<sup>2</sup>

(125 km<sup>2</sup> / 100,000 km<sup>2</sup>) = **0.13% of area occupied  
by “foot prints” of drill sites**

## GULF OF MEXICO GAS AND OIL FIELDS



20% of sites

$$(25 \text{ km}^2) \times (3 \times 10^{10} \text{ g/km}^2) \times (2.5 - 0.44 \text{ ng MeHg/g sed.}) = \underline{1545 \text{ g MeHg}}$$

Sediment in top 2 cm over 1 km<sup>2</sup>

$$(99975 \text{ km}^2) \times (3 \times 10^{10} \text{ g/km}^2) \times (0.44 \text{ ng MeHg/g sed.}) = \underline{1,320,000 \text{ g MeHg}}$$

$(1,320,000/1,321,545) > 99.9\%$  of all MeHg in  
**OCS sediments not tied to oil and gas activities.**

